

VI.—*On Nitroso- $\beta$ -Naphtholsulphonic Acid.*

By RAPHAEL MELDOLA.

THE ideas which have prompted the investigation which has led to the discovery of this nitroso-sulphonic acid are briefly as follow:—

The colouring-matters described in the preceding paper are, as already stated, of but little value as dye-stuffs, and it therefore became of interest to investigate the derivatives of these bodies containing acid radicles, it being now well known that the tinctorial value of the “diazo-colours” is greatly increased by the introduction of one or more such radicles into one or both of the aromatic nuclei linked together by the diazo-group. As the “ $\beta$ -naphthol violet” did not appear to readily form a sulphonic acid by the direct action of sulphuric acid upon it, I was led to investigate the action of nitrous acid upon the sulphonic acids of the naphthols, with a view to producing by this means the nitroso-sulphonic acids, which would furnish a

means of forming bodies of the type of the " $\beta$ -naphthol violet" containing the group  $\text{HSO}_3$ .

When a solution of sodium nitrite is mixed with a solution of a salt of  $\beta$ -naphtholsulphonic acid, the two salts being in exact molecular proportions, on adding dilute  $\text{HCl}$  to the well-cooled mixture, a solution of a deep orange colour is formed, and no trace of nitrous gas is evolved. These facts led me to believe that some definite reaction had taken place, and on adding to the orange solution a large excess of caustic soda a green colour was produced, and on standing in the cold for some time, minute green needles of the sodium salt of nitroso- $\beta$ -naphtholsulphonic acid separated out. The extreme solubility of this sodium salt in water, the readiness with which it decomposes on evaporating the solution on a water-bath, and the difficulty of isolating in a state of purity a substance requiring excess of caustic soda for its precipitation, led me to seek for some other method of obtaining a salt fit for analysis. This process, which will be described later on, is based upon the insolubility of the Ba or Ca salt of the new acid.

The  $\beta$ -naphtholsulphonic acid employed in these experiments was prepared from commercial  $\beta$ -naphthol purified by distillation and crystallisation from toluene till it possessed a melting point of  $122^\circ$ . This  $\beta$ -naphthol was mixed with about 2–3 times its weight of strong sulphuric acid, and heated on a water-bath for about half an hour. As the free acid was not required, the contents of the flask were poured into a large bulk of water, neutralised with milk of lime, boiled, and filtered. The calcium salt was then converted into the ammonium salt by decomposition with ammonium carbonate and filtering off the calcium carbonate. The filtrate on cooling deposits a certain amount of the ammonium salt, and a further quantity can be obtained by evaporating the mother liquor. The ammonium salt was chosen because of the readiness with which it crystallises, and the ease with which it can thus be obtained in a state of perfect purity.

*Ammonium  $\beta$ -naphtholsulphonate* crystallises in long flat transparent prisms with pointed extremities, or, when a large bulk of the solution is allowed to cool slowly, in large plates sometimes half an inch in length. Analysis showed it to possess the formula  $\text{C}_{10}\text{H}_7\cdot\text{HO}\cdot\text{NH}_4\text{SO}_3$ . At  $24^\circ$  100 parts of water dissolve nearly 3 parts of the salt. The latter is very stable, and can be boiled with dilute sulphuric or hydrochloric acid without parting with its ammonium group.

*Barium Nitroso- $\beta$ -Naphtholsulphonate.*

To prepare this salt 16–18 parts of distilled water are poured upon one part of the finely powdered ammonium salt, and a standard solu-

tion of sodium nitrite added in the proportion of one molecule of the latter salt to one of the sulphonate. Dilute hydrochloric acid is then gradually poured into the well-cooled solution till it shows a strongly acid reaction, and all the ammonium salt has dissolved. The deep orange solution is then made alkaline with ammonia, and barium chloride solution added as long as a precipitate forms. The latter is collected on a filter, where it remains as a bright green paste, which is well washed, first with cold and finally with boiling water, till a few drops of the filtrate no longer give a crimson colour on the addition of dilute hydrochloric or sulphuric acid. The green paste is then transferred to a flask and agitated with dilute hydrochloric acid, which changes its colour to orange, and on standing for some time a heavy crystalline deposit settles down, which is collected and washed with cold water. Both the green paste and orange crystals are barium salts of nitroso- $\beta$ -naphtholsulphonic acid, and will be designated by their respective colours. The orange salt may be purified by two or three crystallisations from boiling water, or, in cases where there is much associated impurity, the hot aqueous solution may be precipitated by ammonia, and the green salt collected, washed, and again converted into the orange salt by dilute hydrochloric acid, and recrystallised.

*Analyses of Orange Ba salt.*

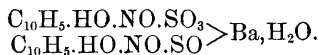
- I. 0.4944 gram dissolved in hot water and decomposed by  $\text{H}_2\text{SO}_4$  gave 0.1742 gram  $\text{BaSO}_4$ .
- II. 0.5914 gram gave 0.2097 gram  $\text{BaSO}_4$ .
- III. 0.3309        „        0.1168        „
- IV. 0.8440 gram fused with  $\text{KHO}$  and  $\text{KNO}_3$  gave 0.5852 gram  $\text{BaSO}_4$ .
- V. 0.3675 gram fused as above gave 0.2670 gram  $\text{BaSO}_4$ .
- VI. 0.2951 gram dried at  $100^\circ$ , burnt with lead chromate gave 0.0632 gram  $\text{H}_2\text{O}$  (1 mol. of water of crystallisation subtracted) and 0.3930 gram  $\text{CO}_2$ .

*Water of Crystallisation.*

- VII. 0.7153 gram dried at  $100^\circ$ , and heated in an air-bath to  $140$ — $150^\circ$  till the weight was constant, lost 0.0171 gram  $\text{H}_2\text{O}$ .
- VIII. 0.6453 gram treated as above lost 0.0168 gram  $\text{H}_2\text{O}$ .

	Theory.		Found (mean).
C <sub>20</sub> .....	240	36.41	36.32
H <sub>12</sub> .....	12	1.82	2.37
N <sub>2</sub> .....	28	4.25	—
O <sub>10</sub> .....	160	24.30	—
S <sub>2</sub> .....	64	9.71	9.74
Ba.....	137	20.78	20.76
H <sub>2</sub> O.....	18	2.73	2.49
	<hr/>	<hr/>	
	659	100.00	

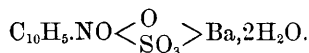
These results show that the orange salt has the formula :—



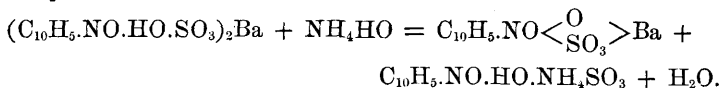
A determination of Ba in a specimen of the anhydrous salt dried at 140—150° gave 21.33 per cent.; theory requiring 21.37.

The orange salt crystallises in large tufts of flattened needles with a golden lustre, crystals nearly three-quarters of an inch long having sometimes been obtained by the slow crystallisation of a large bulk of the solution. It is but very sparingly soluble in cold water; at 30° 100 parts of water dissolve about two parts of the salt.

The green Ba salt was prepared for analysis by dissolving the orange salt in a considerable quantity of hot water, and adding ammonia. The bright green bulky precipitate thus obtained was seen under the microscope to consist of minute needle-shaped crystals. Analysis showed it to possess the formula :—



The action of an alkali upon the orange salt is therefore represented by the equation :—



The ammonium nitroso- $\beta$ -naphtholsulphonate formed in this reaction is most obstinately retained by the green Ba salt, so that for the purposes of analysis it was found necessary to add sufficient BaCl<sub>2</sub> to the ammoniacal solution to decompose the whole of the ammonium salt present. The green salt is then collected and well washed with boiling water, in which it is practically insoluble.

#### *Analysis of Green Ba Salt.*

- I. 0.370 gram (dried at 100°) gave on decomposition with dilute H<sub>2</sub>SO<sub>4</sub> 0.2039 gram BaSO<sub>4</sub>.

44 MELDOLA ON NITROSO- $\beta$ -NAPHTHOLSULPHONIC ACID.

- II. 0.6156 gram fused with KHO and  $\text{KNO}_3$  gave 0.3396 gram  $\text{BaSO}_4$ .  
 III. 0.3029 gram (dried at  $100^\circ$ ) burnt with lead chromate gave 0.3153 gram  $\text{CO}_2$  and 0.0422 gram  $\text{H}_2\text{O}$  (water of crystallisation subtracted).

*Water of Crystallisation.*

- IV. 0.5198 gram dried at  $100^\circ$ , and in an air-bath to  $240-250^\circ$  till the weight was constant, lost 0.0438 gram  $\text{H}_2\text{O}$ .  
 V. 0.4056 gram treated as above lost 0.0354 gram  $\text{H}_2\text{O}$ .

	Theory.		Found.
$\text{C}_{10}$ .....	120	28.30	28.39
$\text{H}_5$ .....	5	1.17	1.54
$\text{N}$ .....	14	3.30	—
$\text{O}_5$ .....	80	18.88	—
$\text{S}$ .....	32	7.55	7.37
$\text{Ba}$ .....	137	32.31	32.37
$2\text{H}_2\text{O}$ .....	36	8.49	8.57 (mean)
	<hr/> 424	<hr/> 100.00	

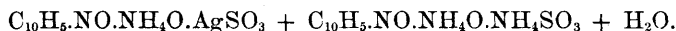
The water of crystallisation is not given off completely till the salt is heated to the temperature mentioned above ( $240-250^\circ$ ), when partial decomposition takes place, but the weight remains constant as long as this temperature is not exceeded.

Nitroso- $\beta$ -naphtholsulphonic acid thus forms two classes of salts represented by the green and orange Ba salts. In cases where large quantities of a salt of this acid are required, calcium chloride can be used for precipitating the ammoniacal solution of the acid after its first formation from ammonium  $\beta$ -naphtholsulphonate by the action of nitrous acid ( $\text{NaNO}_2$  and  $\text{HCl}$ ).

By decomposing a solution of the Ba salt with an equivalent quantity of  $\text{H}_2\text{SO}_4$  and evaporating the solution in a vacuum, the free acid was obtained in microscopic orange nodular crystals, extremely soluble in water, and decomposed by heating to a very moderate temperature in a dry tube, so that its melting point could not be determined.

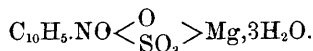
Of the other salts of nitroso- $\beta$ -naphtholsulphonic acid I have prepared the following:—

*Silver ammonium* (double) salt formed by adding  $\text{AgNO}_3$  to a solution of the ammonium salt of nitroso- $\beta$ -naphtholsulphonic acid in the presence of an excess of ammonia. Dull olive-green microscopic needles decomposed by boiling water. Analysis gave the formula:—



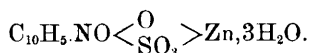
Found, 15.87 per cent. Ag, 9.69 per cent. S; theory, 15.83 per cent. Ag, 9.38 per cent. S.

*Magnesium salt*, formed by decomposing the orange Ba salt with an equivalent (2 mols.) of  $\text{MgSO}_4$ , and adding ammonia to filtrate. Dull orange needles moderately soluble in cold, readily soluble in boiling, water. Analysis gave the formula:—



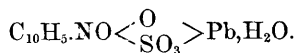
Found, 7.27 per cent. Mg, 16.70 per cent.  $\text{H}_2\text{O}$ ; theory, 7.29 per cent. Mg, 16.41 per cent.  $\text{H}_2\text{O}$ . Water of crystallisation not given off till  $250^\circ$ .

*Zinc salt*, formed in the same manner as the Mg salt. Large scaly crystals, dull green by reflected light, orange by transmitted light. Moderately soluble in cold water, more readily soluble in hot water. Analysis gave the formula:—



Found, 17.81 per cent. Zn, 8.86 per cent. S, and 14.62 per cent.  $\text{H}_2\text{O}$ ; theory, 17.56 per cent. Zn, 8.64 per cent. S, 14.59 per cent.  $\text{H}_2\text{O}$ . Water of crystallisation only given off completely at  $280^\circ$  with partial decomposition of the salt.

*Lead salt* precipitated on adding a solution of lead acetate to a solution of the sodium or ammonium salt of nitroso- $\beta$ -naphtholsulphonic acid acidulated with acetic acid. Minute ochreous needles insoluble in boiling water. Analysis gave the formula:—



Found, 43.60 per cent. Pb; theory, 43.48 per cent. Pb. No loss of water at  $250^\circ$ .

*Copper Salts*.—On adding a solution of  $\text{CuSO}_4$  to a solution of the free nitroso-sulphonic acid containing an excess of  $\text{H}_2\text{SO}_4$ , a bulky brown gelatinous precipitate, almost insoluble in boiling water, separates out. On suspending this gelatinous salt in cold water and adding ammonia a double copper-ammonium salt settles down after some hours in the form of small brown glistening scales. The constitution of this salt has not been determined. Analysis gave 17.92 per cent. Cu and 8.55 per cent. S.

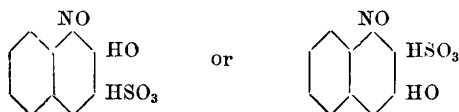
An attempt was made to prepare an acetyl derivative of nitroso- $\beta$ -naphtholsulphonic acid by acting upon the sodium salt of acetyl- $\beta$ -naphtholsulphonic acid with sodium nitrite and dilute hydrochloric acid, but the acetyl-group appears to be eliminated in the course of the reaction, as on adding ammonia and barium chloride the ordinary

green Ba salt was precipitated. An attempt to prepare a nitroso-derivative of methyl- $\beta$ -naphthol in a similar manner was also unsuccessful.

Nitroso- $\beta$ -naphtholsulphonic acid is very easily decomposable. The nitroso-group is readily reducible by any reducing agent, but I have not yet been able to obtain the corresponding nitro-sulphonic acid, either by the action of dilute nitric acid or of an alkaline solution of potassium ferricyanide, the molecule apparently completely breaking up under the action of these reagents. On agitating a solution of the nitrososulphonic acid with 1 mol. of bromine the latter is absorbed, but no definitely crystalline brom-nitroso acid was separable.

*Constitution of Nitroso- $\beta$ -Naphtholsulphonic Acid.*

I have made numbers of experiments with a view to determine the constitution of this acid. The free acid when repeatedly evaporated with dilute nitric acid gave no phthalic acid, neither did the nitroso- nor amido-acids when oxidised with an alkaline solution of potassium permanganate. Phthalic acid was, however, obtained by repeatedly evaporating the amido-acid with dilute nitric acid. This result is of interest as showing that in nitroso- and amido- $\beta$ -naphtholsulphonic acid all these substituents are in the same benzene-ring. In their recently published monograph upon naphthalene Reverdin and Nölting ("Ueber die Constitution des Naphtalins und seiner Abkömmlinge," Genf., 1880, p. 25) assign to  $\beta$ -naphtholsulphonic acid a formula in which the  $\text{HSO}_3$  and  $\text{HO}$ -groups are in different benzene-nuclei, but no reasons are assigned for adopting this constitution. In a communication to this Society last November Armstrong gave reasons for believing that in this acid the two substituents are both in the same benzene-ring, being in the two  $\beta$ -positions. Although I have made repeated attempts to confirm this view by oxidising  $\beta$ -naphtholsulphonic acid with an alkaline solution of permanganate, I have not succeeded in obtaining phthalic acid from this compound. The production of phthalic acid, however, from amido- $\beta$ -naphtholsulphonic acid in the manner above described goes to support Armstrong's view of the constitution of this sulphonic acid, and shows that the nitroso-acid has the constitution:—



Among the reactions of nitroso- $\beta$ -naphtholsulphonic acid which I have investigated the most interesting appears to be that with the phenols and certain primary and secondary monamines. The phenol or amine is dissolved in glacial acetic acid, the finely powdered barium or calcium salt of the nitroso-acid added, and after the addition of a small quantity of sulphuric acid the mixture is warmed. The following colouring-matters have been obtained in this manner:—

*Resorcinol* and ordinary *phenol* give a deep blue, changing to red on dilution with water.

*Diphenylamine* gives a similar blue, which retains its colour on dilution, but becomes red on neutralising with an alkali.

*Benzyl- $\alpha$ -naphthylamine* gives a fine red, which is not changed by dilution.

These bodies are probably built on the type of the  $\beta$ -naphthol-violet described in the last paper, and containing  $\text{HSO}_3$  in the naphthalene-group. Their value as dyes does not appear, however, to be increased by the presence of the acid radicle. I hope to investigate these substances more fully at a future period.

On mixing solutions of ammonium nitroso- $\beta$ -naphtholsulphonate and ammonium sulphite, and allowing the mixture to stand for some hours in the cold, white scaly crystals separate out, which have not yet been further investigated.

#### *Amido- $\beta$ -naphtholsulphonic Acid.*

This acid was prepared by boiling a solution of the nitroso-acid with tin and hydrochloric acid, removing the tin by sulphuretted hydrogen and evaporating the cold solution in a vacuum. The acid then separates out in the form of long white needles, which after one or two washings with cold water are sufficiently pure for analysis:—

0.2380 gram fused with  $\text{KHO}$  and  $\text{KNO}_3$  gave 0.2380 gram

$\text{BaSO}_4 = 13.73$  per cent. S.

0.4984 gram gave 0.4928 gram  $\text{BaSO}_4 = 13.57$  per cent. S.

Theory for $\text{C}_{10}\text{H}_5\text{.NH}_2\text{.HO.HSO}_3$ .		Found (mean).
S. ....	13.38	13.65

Amido- $\beta$ -naphtholsulphonic acid is readily soluble in water. Its aqueous solution, and especially that of its salts, oxidises on exposure to the air, and turns brown. A hot solution undergoes this change rapidly. The melting point of the acid could not be determined, as it decomposes on heating.

In concluding this paper I may take the opportunity of announcing that I have recently succeeded in obtaining an iodine derivative of  $\beta$ -naphthol by acting upon this substance dissolved in glacial acetic



acid with iodine in the presence of lead acetate. I hope shortly to lay before the Society an account of this substance and some of its derivatives. It is also my pleasing duty to express my thanks to the firm of Brooke, Simpson, and Spiller, in whose laboratory at the Atlas Works these investigations have been conducted.

---