

parts of water at 20°, in eighty-six parts of boiling water, in forty-seven parts of cold alcohol, in fifteen parts of hot alcohol, and in forty-five parts of ether.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CINCINNATI.]

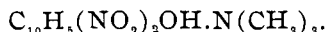
LVII. ON CERTAIN AMINE DERIVATIVES OF DINITRO- α -NAPHTHOL AND ITS CHLORINATION.

By T. H. NORTON AND IRWIN J. SMITH.

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IN connection with a recent study of dinitro- α -naphthol derivatives,¹ the following salt of this phenol with various amines were prepared and analyzed. The dinitro- α -naphthol used was prepared from the commercial calcium salt by treatment with sulphuric acid and recrystallization from alcohol. It possessed the correct melting-point of 138°.²

TRIMETHYLAMINE-DINITRO- α -NAPHTHOLATE,



This salt was prepared by boiling dinitro- α -naphthol with an excess of a thirty-three per cent. aqueous solution of trimethylamine. The product was crystallized from alcohol and obtained in the form of long, lustrous, red needles, which are anhydrous and melt at 190° (uncorr.). The salt is soluble in 909 parts of water at 18°, in fifteen parts at 100°, in 200 parts of cold alcohol, in 40 parts of boiling alcohol, and in 4,000 parts of ether. It is insoluble in carbon disulphide and in benzene. The temperature of solutions in all cases, when not otherwise noted, is 18° C.

Analysis: 0.2154 gram of the salt dried at 100° gave 0.0969 gram water or five per cent. of hydrogen, and 0.4193 gram carbon dioxide or 53.06 per cent. of carbon.

	Theory.	Found.
Carbon	53.24	53.06
Hydrogen	5.12	5.00

The yellow solutions of the salt resemble in tinctorial power those of dinitro- α -naphthol itself.

¹ Norton and Loewenstein: This Journal, 19, 923.

² Martius: *Ztschr. Chem.*, 1868, 80.

ANILINE-DINITRO- α -NAPHTHOLATE,
 $C_{10}H_6(NO_2)_2OH.NH_2(C_6H_5)$.

This salt was prepared by boiling together in molecular proportions, aniline and dinitro- α -naphthol in alcoholic solution. The resultant solution was allowed to crystallize by spontaneous evaporation, and the crude product was recrystallized from alcohol three times before a constant melting-point was attained. The salt thus prepared is obtained in the form of light yellow, fine, acicular crystals united in rosettes, which melt at 129° . It is naturally anhydrous. It dissolves in 72,000 parts of water, in 264 parts of boiling water, in 200 parts of cold alcohol, in 130 parts of boiling alcohol, in 100 parts of ether, in 814 parts of carbon disulphide, and in 16,600 parts of benzene. The solutions are of a yellow color, and dye strongly.

Analysis: The salt lost no weight on heating to 100° . 0.0855 gram of the salt dried at 100° , gave 0.0285 gram of water or 3.71 per cent. of hydrogen, and 0.168 gram of carbon dioxide, or 53.59 per cent. of carbon.

	Theory.	Found.
Carbon	53.80	53.59
Hydrogen	3.62	3.71

ORTHOTOLUIDINE-DINITRO- α -NAPHTHOLATE,
 $C_{10}H_6(NO_2)_2OH.NH_2.C_6H_4.CH_3$.

The preparation is similar to that of the aniline salt. It crystallizes in fine, silky, yellow needles, usually united in rosettes, which are anhydrous and melt at 132° . It is soluble in 6,800 parts of water, in 614 parts of boiling water, in fifty-two parts of cold alcohol, in seven and a half parts of boiling alcohol, in 60 parts of ether, and in 288 parts of carbon disulphide. It is insoluble in benzene. The tinctorial properties are similar to those of the aniline salt.

Analysis: 0.1635 gram of the salt dried at 100° gave 0.072 gram of water or 4.80 per cent. of hydrogen, and 0.3624 gram of carbon dioxide or 60.42 per cent. of carbon.

	Theory.	Found.
Carbon	59.82	60.42
Hydrogen	4.40	4.80

DIMETHYL-ANILINE-DINITRO- α -NAPHTHOLATE,
 $C_{10}H_6(NO_2)_2OH.N(CH_3)_2C_6H_5$.

The preparation is similar to that of the aniline salt above. It is obtained in the form of lustrous, large, thin, flat crystals of a yellowish-brown color, which are anhydrous and melt at 115° . It dissolves in 8,580 parts of water at 20° , in 455 parts of boiling water, in 255 parts of cold alcohol, in ten parts of hot alcohol, in 67.5 parts of ether, and in ninety parts of carbon disulphide. It is insoluble in benzene. The tinctorial properties are similar to those of the aniline salt.

Analysis: 0.0325 gram of the salt dried at 100° gave 0.7281 gram carbon dioxide or 61.07 per cent. carbon, and 0.0143 gram water or 4.89 per cent. hydrogen.

	Theory.	Found.
Carbon	60.86	61.07
Hydrogen	4.78	4.89

NOTE ON THE CHLORINATION OF DINITRO- α -NAPHTHOL.

The following work was undertaken with the view of ascertaining whether the nitro group in aromatic compounds can be directly replaced by chlorine. Lellmann, in his *Principien der organischen Chemie*, states that there is no such case on record. The results of our experiments would tend to show that this substitution can take place, although they are not fully satisfactory.

Carefully purified dinitro- α -naphthol was placed in a U-tube immersed in a beaker of water, and was connected with a generator yielding dry chlorine. The temperature was maintained at 100° . The contents of the tube soon changed to a dull red, viscous mass, through which the gas bubbled. The color gradually deepened as chlorine was absorbed. The operation was continued for some days until there was no further increase in weight. 5.519 grams gained thus 0.364 gram in weight, or six and six-tenths per cent. The substance thus obtained was, when cold, of a dark yellow and viscous. It was slightly soluble in ether, alcohol, carbon disulphide, and benzene. From none of these solutions, however, could crystals be secured, nor could a distinct melting-point be obtained from any of the residues left on evaporation. A qualitative analysis showed the absence of nitrogen. A chlorine determination gave :

	Per cent.
Chlorine	21.77

Monochlor naphthol requires 19.66 per cent. ; dichlor naphthol requires 33.02 per cent. There was evidently no simple substitution of Cl for NO₂, and it was plain that more complicated changes than those involved by substitution had taken place. The inability to obtain a product offering the assurance of purity, caused a discontinuance of the work. The expulsion of the nitro group by chlorine under these conditions, is, however, worthy of note.

THE RATE OF SOLUTION OF SOLID SUBSTANCES IN THEIR OWN SOLUTIONS.

BY ARTHUR A. NOYES AND WILLIS R. WHITNEY.

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AS far as we know, the effect of the concentration on the rate at which a solid substance dissolves in its own solution, has not heretofore been investigated. This is probably due to the experimental difficulties in the way of keeping the surface of the dissolving substance constant during the solution.

The question is an important one, especially because of the light its solution would throw upon the attainment of the state of saturation, which is a matter of importance in all solubility determinations. Therefore we have investigated the phenomenon and have succeeded in experimentally establishing the law according to which the process takes place.

The experiments were carried out in the following manner : In order to keep the alteration of the surface-area of the dissolving substances as small as possible, the slightly soluble substances, benzoic acid and lead chloride, were chosen. Cylinders of these two substances, about eight cm. long and two in diameter, were prepared upon cores of glass. In the case of benzoic acid, this was done by simply pouring the melted acid into a test-tube containing a glass rod flattened a little at the lower end and protruding at the other end above the test-tube. When the whole had cooled, the cylinder of acid adhering well to the glass rod could usually be easily removed from the tube. It was found necessary in the case of lead chloride to proceed differ-