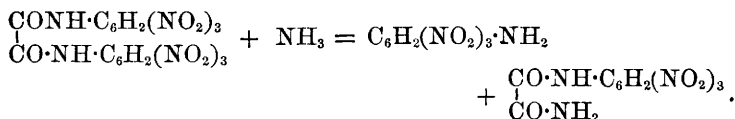


LXXVI.—*Hexanitroxanilide*.

By A. G. PERKIN, F.R.S.E.

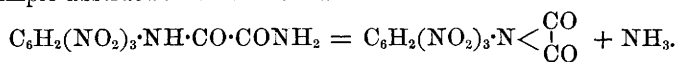
IN a previous communication "On the Action of Nitric Acid on Oxanilide and its Homologues" (Trans., 1892, **61**, 458), it was shown that, when treated with fuming nitric acid, this substance yields di- and tetra-nitroxanilides, but that, when a mixture of fuming nitric and sulphuric acids is employed, hexanitroxanilide is formed.

These substances differ in a somewhat remarkable way in their behaviour towards ammonia, both di- and tetra-nitroxanilide being converted by this agent into mono- and di-nitraniline and oxalic acid respectively, whilst but very little trinitraniline is obtained from hexanitroxanilide, the principal product being a colourless, crystalline substance, which, at the time, was not further investigated. Considerable quantities of hexanitroxanilide have since been prepared, and it has been found that the products of the action of ammonia on it are, in the first instance, trinitraniline and the ammonium salt of a substance which appears to be the amide of trinitroxanilic acid, thus,

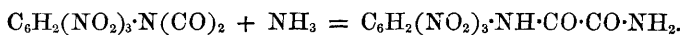


It forms beautiful sodium, potassium, and ammonium derivatives, which crystallise in red leaflets having a magnificent golden lustre. If the substance has the constitution given to it above, the sodium derivative, for example, would be represented by the formula $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{NNa}\cdot\text{CO}\cdot\text{CONH}_2$. The analytical results agree well with this assumption. When heated with hydrochloric acid under pressure at 160° , trinitrophenyloxamide is resolved into trinitraniline and oxalic acid, and concentrated sulphuric acid acts on it in a similar manner.

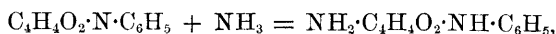
A cold mixture of fuming nitric and sulphuric acids converts it into a new substance which is probably trinitroxanil, formed, apparently, by simple abstraction of ammonia.



This explanation is rendered the more probable from the fact that the product in question, when treated with ammonia, is reconverted into trinitrophenyloxamide.



This action is somewhat analogous to the conversion of succinil into phenylsuccinamide by the action of alcoholic ammonia (Menschutkin, *Annalen*, **162**, 182),



and the reconversion of the latter into succinil and ammonia by the aid of heat.

When heated with hydrochloric or sulphuric acid at a high temperature, trinitroxanil yields trinitraniline.

Attempts to produce higher nitrated compounds from hexanitroxanilide were unsuccessful, the substance being very slowly attacked at about 200°, and converted into trinitrobenzene [$\text{NO}_2 : \text{NO}_2 : \text{NO}_2 = 1 : 3 : 5$] melting at 121°.

Similar experiments with dinitroxalorthotoluidide resulted in the production of dinitrotoluene [$\text{CH}_3 : \text{NO}_2 : \text{NO}_2 = 1 : 3 : 5$], but in the case of dinitroxalparatoluidide the action proceeded differently, dinitrobenzoic acid being formed as principal product.

In this paper, an account is also included of the preparation and properties of hexanitrocarbanilide, these experiments having been at first instituted with the object of determining whether this substance on treatment with ammonia would give products in any way similar to those obtained from hexanitroxanilide. Hexanitrocarbanilide is readily obtained by the action of a mixture of nitric and sulphuric acids on tetranitrocarbanilide, in the form of colourless, minute prisms, which, when treated with sodium or potassium hydrate, yield well-crystallised salts. Treatment with ammonia readily converts it into trinitraniline, and no intermediate products could be obtained.

Action of Ammonia on Hexanitroxanilide.

Hexanitroxanilide was added to a large excess of concentrated aqueous ammonia, diluted with 2 parts of water, in which it readily dissolved, forming an orange-coloured solution, from which acids reprecipitated the substance unchanged. On heating the liquid to the boiling point, it became dark red, and a small quantity of a crystalline substance gradually separated. This was collected, washed with water, and crystallised from glacial acetic acid; the yellow needles thus obtained melted at 186° and had the properties of trinitraniline.

The filtrate while still hot was nearly neutralised with concentrated hydrochloric acid, and the glittering red leaflets which separated, and which increased in quantity as the liquid cooled, were collected, made into a thin paste with hot water, and treated with hydrochloric acid; a nearly colourless, crystalline precipitate, seen under the microscope

to consist of minute, flat needles, was obtained. After filtration, washing with water, and pressing, the substance was ultimately purified by crystallisation from nitrobenzene with the aid of animal charcoal. It was analysed with the following results.

0.1352 gave 0.1611 CO_2 and 0.0262 H_2O . $\text{C} = 32.49$; $\text{H} = 2.15$.
 0.1504 „ 0.1784 CO_2 and 0.0307 H_2O . $\text{C} = 32.34$; $\text{H} = 2.26$.
 0.1258 „ 26 c.c. moist nitrogen at 21° and 760 mm. $\text{N} = 23.62$.
 0.1333 „ 27 c.c. „ „ 19° and 762 mm. $\text{N} = 23.34$.
 0.1264 „ 25.8 c.c. moist nitrogen at 23° and 757 mm. $\text{N} = 22.92$.
 $\text{C}_6\text{H}_2(\text{NO}_2)_3\text{NH}\cdot\text{CO}\cdot\text{CONH}_2$ requires $\text{C} = 32$; $\text{H} = 2$; $\text{N} = 23.3$ p. c.

Trinitrophenyloxamide is deposited from its hot solution in nitrobenzene as a colourless mass of glistening needles, which melt at 257° , gas being evolved, and which, when strongly heated, suddenly decompose, a black vapour being given off. It is almost insoluble in benzene and xylene, but readily soluble in methyl and ethyl alcohols, hot concentrated solutions of which deposit it in a gelatinous condition. By crystallisation from acetic anhydride, it can be obtained in the form of long needles, but continued heating with this solvent converts it into a very soluble product, which could not be obtained in a crystalline condition. Heated at 160° in a sealed tube with hydrochloric acid, it is converted into a mass of long, yellow needles melting at 186° , and consisting of trinitraniline; concentrated sulphuric acid at 160° decomposes it in a similar way.

Trinitrophenyloxamide is readily dissolved by aqueous solutions of potassium hydrate, forming a blood-red solution of the potassium salt, and this is most readily obtained in a crystalline condition by partially neutralising the boiling alkaline solution with acetic acid. On cooling, the liquid gradually deposits beautiful, glistening, scarlet leaflets, having a golden lustre; these were collected and dried over sulphuric acid until constant in weight. The salt contains no water of crystallisation.

0.4898 heated with H_2SO_4 gave 0.1298 K_2SO_4 . $\text{K} = 11.87$.

$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{NK}\cdot\text{CO}\cdot\text{CONH}_2$ requires $\text{K} = 11.5$ per cent.

Potassium trinitrophenyloxamide dissolves sparingly in alcohol and water, but is readily soluble in alkaline liquids, the solutions so formed being gradually decomposed on long boiling, with evolution of ammonia. If heated in a test-tube, it suddenly decomposes, a slight explosion taking place.

Sodium trinitrophenyloxamide can be prepared in a manner similar to the potassium salt, with which in its properties and appearance it is almost identical. It contained no water of crystallisation.

0.1827 gave 34.2 c.c. moist nitrogen at 15° and 760 mm. N = 21.92.
 0.2100, on ignition with H_2SO_4 gave 0.0475 Na_2SO_4 . Na = 7.24.
 0.2373 " " " 0.0515 Na_2SO_4 . Na = 7.03.
 0.3078 " " " 0.0618 Na_2SO_4 . Na = 6.50.
 $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{NNa} \cdot \text{CO} \cdot \text{CONH}_2$ requires N = 21.8; Na = 7.14 per cent.

Ammonium trinitrophenyloxamide crystallises in thin scales, having a somewhat greener iridescence than the potassium and sodium salts, but resembles it closely in most of its properties. When it is heated in the oil-bath, ammonia is evolved, leaving a colourless residue of the original substance.

0.1420 gave 32.5 c.c. moist nitrogen at 12° and 760 mm. N = 27.16.
 $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{N}(\text{NH}_4) \cdot \text{CO} \cdot \text{CONH}_2$ requires N = 26.58 per cent.

Trinitroxanil.

Trinitrophenyloxamide, when added to a cold mixture of equal parts of nitric acid (sp. gr. 1.5) and sulphuric acid, at once dissolves, but, after a few seconds, the liquid rapidly sets to a stiff, colourless mass of minute, hair-like needles.

In order to purify this product, it was drained on a porous tile for several hours, washed first with a little glacial acetic acid, and then several times with a mixture of chloroform and glacial acetic acid, and finally crystallised two or three times from methyl alcohol.

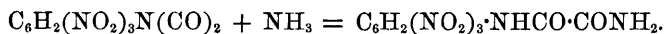
0.1403 gave 23.4 c.c. moist nitrogen at 12° and 764 mm. N = 19.9.
 0.1421 " 23.3 c.c. " " 12° and 764 mm. N = 19.56.
 $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{N}(\text{CO})_2$ requires N = 19.85 per cent.

Trinitroxanil crystallises from methyl alcohol as a colourless mass of thin, glistening plates, which melt at 146°. It is very soluble in nitrobenzene, readily so in alcohol and ether, but only sparingly in water. The solution in water is exceedingly bitter. When heated in a sealed tube at 200° with hydrochloric acid, it yields trinitraniline. Strong sulphuric acid at 160° acts similarly on it. When boiled with a mixture of nitric and sulphuric acids, it is decomposed, and, on the addition of water, a clear solution is formed, from which nothing could be extracted by means of ether.

Trinitroxanil readily dissolves in cold ammonia, forming an orange-solution, which quickly changes to a deep red. The addition of hydrochloric acid causes the separation of a scarlet, crystalline precipitate, which, when again treated with acid, is gradually converted into a colourless, crystalline mass; this was collected, washed with water, and purified by crystallisation from nitrobenzene.

0.1563 gave 32.4 c.c. moist nitrogen at 18° and 746 mm. N = 23.49.
 0.1455 „ 29.5 c.c. „ „ 14° and 752 mm. N = 23.59.
 0.1465 „ 0.1743 CO₂ and 0.0260 H₂O. C = 32.48; H = 1.96.
 C₆H₂(NO₂)₃·NH·CO·CONH₂ requires C = 32.00; H = 2.00; N = 23.33 per cent.

It is, therefore, trinitrophenyloxamide, and its formation from trinitroxanil may be represented by the equation



Decomposition of Hexanitroxanilide by means of Nitric and Sulphuric acids.

As previously stated (Trans., 1892, **61**, 462), when this substance is heated at 200° in a sealed tube with a mixture of nitric acid (sp. gr. 1.5) and sulphuric acid during three hours, no higher nitro-derivative is produced, the greater portion of the hexanitroxanilide remaining unchanged. It was found, however, that by very prolonged heating at a slightly higher temperature, the hexanitroxanilide is gradually decomposed, a more soluble product being formed.

5 grams of hexanitroxanilide were added to a mixture of 50 c.c. of sulphuric acid and 10 c.c. nitric acid of sp. gr. 1.5, in a large flask, and gradually heated, frequently shaking. As the temperature rose, nitrous fumes were evolved, accompanied by considerable frothing, which, after the bulk of the nitric acid had evaporated, gradually subsided, leaving a clear solution. This was at once poured into much water, the yellow liquid extracted two or three times with ether, the extract well washed with water, evaporated, and the crystalline residue drained on a porous plate. This product was best purified by boiling for a short time with fuming nitric acid, in which it dissolved, and the fern-like crystals, which were deposited from the solution on cooling, were then crystallised two or three times from alcohol.

0.1212 gave 20.4 c.c. moist nitrogen at 14° and 764 mm. N = 19.91.
 0.1242 „ 21 c.c. „ „ 14° and 760 mm. N = 19.89.
 0.1164 „ 19.5 c.c. „ „ 13° and 764 mm. N = 19.89.
 C₆H₃(NO₂)₃ requires N = 19.71 per cent.

This substance melts at 121°, and is identical with the trinitrobenzene [(NO₂)₃ = 1 : 3 : 5], prepared by Hepp (*Annalen*, **215**, 345).

To confirm this result, a portion of the substance was converted into its aniline compound by the addition of aniline to its alcoholic solution.

0.0594 gave 9.5 c.c. moist nitrogen at 12° and 748 mm. N = 18.68.
 C₆H₃(NO₂)₃·C₆H₅·NH₂ requires N = 18.30 per cent.

This aniline compound forms reddish-yellow, prismatic needles, which are readily decomposed at 100° , aniline being given off.

Tetranitroxalorthotoluidide, when treated with a mixture of nitric and sulphuric acids, in the manner described in the case of hexanitroxanilide, is decomposed somewhat more readily than the latter. An ethereal extract of the acid solution, on evaporation, leaves a thick, brown oil, which gradually becomes crystalline when treated with a little methyl alcohol. After purification, it is obtained in yellow needles melting at 91° , and evidently identical with the dinitrotoluene $[\text{CH}_3\cdot\text{NO}_2\cdot\text{NO}_2 = 1:3:5]$ prepared by Stadel (*Annalen*, **217**, 189). The yield was very small, and sufficient of this substance was not obtained for analysis.

Action of Nitric and Sulphuric acids on Tetranitroxalparatoluidide.

In studying the action of nitric and sulphuric acids on tetranitroxalparatoluidide, 3 grams of the tetranitro-compound were mixed with 4 c.c. of fuming nitric acid and 30 c.c. of sulphuric acid, and the mixture treated as already described in the case of hexanitroxanilide.

The ethereal extract of the acid solution, on evaporation, left a brownish, oily residue, which gradually solidified; after draining on a porous plate and washing with chloroform, it was crystallised twice from a mixture of 2 parts of nitric acid and 1 of water. As thus obtained, it consisted of pale yellow, stellate groups, melting at 199° , and having all the properties of dinitrobenzoic acid, $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{COOH}$ $[\text{NO}_2 : \text{NO}_2 : \text{COOH} = 1 : 3 : 5]$.

0.1295 gave 0.1875 CO_2 and 0.0288 H_2O . $\text{C} = 39.48$; $\text{H} = 2.47$.

0.1042 „ 12.4 c.c. moist nitrogen at 23° and 746 mm. $\text{N} = 13.15$. $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{COOH}$ requires $\text{C} = 39.63$; $\text{H} = 1.88$; $\text{N} = 13.20$ p. c.

Hexanitrocarbanilide.

When tetranitrocarbanilide, $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_3\cdot\text{NO}_2)_2$ (Losanitsch, *Ber.*, **10**, 690), is suspended in a mixture of equal parts of nitric acid (sp. gr. 1.5) and sulphuric acid, it does not dissolve, and no action takes place, but, on heating, the needles, without apparently going into solution, become transformed into a mass of minute prisms. As soon as the conversion is complete, the product is poured into a large bulk of water, the precipitate collected, washed with water, and dried at 100° .

An analysis of this product gave the following result.

0.2297 gave 46.3 c.c. moist nitrogen at 14° and 764 mm. $\text{N} = 23.62$.

$\text{CO}[\text{C}_6\text{H}_2(\text{NO}_2)_3\text{NH}]_2$ requires $\text{N} = 23.23$ per cent.

Hexanitrocarbanilide is a colourless, glistening mass, readily soluble in hot nitrobenzene, but only sparingly so in boiling glacial acetic acid. When heated, it melts at 203° , undergoing decomposition, and at higher temperatures is carbonised, a yellow vapour being given off, which condenses to a mass of needles; when crystallised from glacial acetic acid, these melt at 186° , and are evidently trinitraniline. Hexanitrocarbanilide very readily dissolves in a cold aqueous solution of ammonia, and, on gently warming the red solution, it quickly deposits crystals of trinitraniline; all attempts to prepare from the carbanilide a product similar to that obtained, by this means, from hexanitroxanilide were unsuccessful.

The ammonium derivative of hexanitrocarbanilide could not be isolated in a solid condition, but the sodium and potassium derivatives may be readily obtained, in the form of minute, scarlet prisms, by adding it to cold alcoholic solutions of sodium and potassium hydrates. These salts are, however, so readily soluble in alcohol and water that they could not be obtained in a condition pure enough for analysis. They explode on heating, and, on boiling with water, are converted into trinitraniline.

*Clothworkers' Research Laboratory,
Dyeing Department,
Yorkshire College,
Leeds.*
