

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

A STUDY OF 1-HYDROXYLAMINO-ANTHRAQUINONE AND SOME OF ITS DERIVATIVES<sup>1</sup>

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## Introduction

The  $\beta$ -aryl-hydroxylamines as a class are fairly well known. They are usually prepared by the partial reduction of the corresponding nitro compounds. In some cases they appear among the products obtained when primary amines are oxidized and the oxidation is controlled with proper care. The first member of the series,  $\beta$ -phenylhydroxylamine, which may be considered as a typical compound of this class, is of historical importance because of the difficulties early investigators encountered in their attempts to prepare it. In the presence of mineral acids of proper concentration it is readily transformed into *p*-aminophenol, and it was this compound which was usually obtained when  $\beta$ -phenylhydroxylamine might have been expected. It was not until 1894, that Bamberger<sup>2</sup> and Wohl,<sup>3</sup> working independently, succeeded in preparing  $\beta$ -phenylhydroxylamine by the reduction of nitrobenzene in a neutral medium. This may be accomplished by the interaction of aluminum amalgam with an ether solution of nitrobenzene, or by the action of zinc dust upon nitrobenzene suspended in a water solution of some neutral salt, such as ammonium chloride or calcium chloride.<sup>4</sup>

Although anthraquinone derivatives in general have been studied intensively during the past 50 years, very little attention has been paid to the hydroxylamine derivatives, so that the literature on the subject is very meager. Schmidt and Gattermann<sup>5</sup> prepared the 1,5-dihydroxylamino-anthraquinone by the reduction of the 1,5-dinitro compound with a solution of sodium stannite. This compound crystallized in red-brown needles, which dissolved in alkalis with a characteristic blue-green color. No melting point could be determined because of decomposition. Hot, conc. sulfuric acid converts the dihydroxylamino derivative into 1,5-diamino-4,8-dihydroxy-anthraquinone. The dihydroxylamine derivative showed weak base-forming properties; it dissolved in hydrochloric acid to form a solution which was practically colorless and from which it could be recovered unchanged by the addition of water. When an alkaline solution

<sup>1</sup> This paper incorporates a thesis presented by Walter H. Beisler in June, 1922, to the Faculty of the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Science.

<sup>2</sup> Bamberger, *Ber.*, **27**, 1347 (1894).

<sup>3</sup> Wohl, *ibid.*, **27**, 1432 (1894).

<sup>4</sup> Wislicenus, *ibid.*, **29**, 494 (1896).

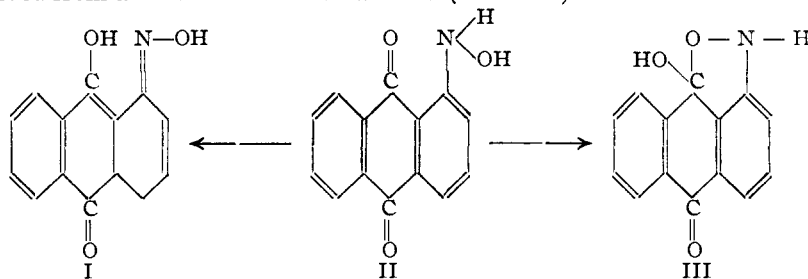
<sup>5</sup> Schmidt and Gattermann, *ibid.*, **29**, 2934 (1896).

of it was shaken with benzoyl chloride, a dibenzoyl derivative melting at 188°, and a tribenzoyl derivative melting at 228° were obtained.

In a similar way, the same investigators obtained 1-hydroxylamino-anthraquinone. It was transformed into 1-amino-4-hydroxy-anthraquinone when it was heated with conc. sulfuric acid.

A little later, Wacker<sup>6</sup> found that 1-nitro-anthraquinone could be reduced to the hydroxylamine derivative by sodium hydrogen sulfide, the cathode action of the electric current, and best, by glucose and alkalis. He also prepared the nitroso-sulfonic acid derivative of anthraquinone by sulfonation of the hydroxylamine derivative and oxidation of the sulfonate in alkaline solution by means of potassium ferricyanide, or by chromic acid. He described the nitroso-sulfonic acid as a yellow-red powder.

The deep color of the hydroxylamine derivatives of anthraquinone and the remarkable change in color produced when these compounds are dissolved in alkalis are properties characteristic only of this particular class of  $\beta$ -hydroxylamine derivatives; it is natural to infer that these unusual properties undoubtedly develop through some influence exerted by the anthraquinone nucleus. The present work was begun with the intention of studying the monohydroxylamine derivative obtained from 1-nitro-anthraquinone in more detail than had previously been done. A study of this kind might be expected to bring to light other irregularities in the behavior of this compound, which could be traced to some influence exerted by the anthraquinone nucleus. In the light of the theories of color, the explanation for the sharp difference in the colors of the free hydroxylamine derivative and its sodium salt should be sought for in differences in structure. The proximity of the carbonyl group to the hydroxylamino group makes such an interpretation seem very satisfactory,—theoretically, at least. If we assume that the free hydroxylamino derivative has the usual structure formula (II) assigned to such compounds, its sodium salt may be derived from at least two other structures (I and III).

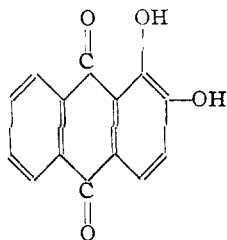


Formula I is in accord with the theory suggested by Georgievics<sup>7</sup> to explain

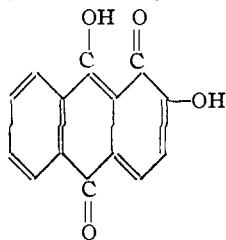
<sup>6</sup> Wacker, *Ber.*, **35**, 666, 3922 (1902).

<sup>7</sup> Georgievics, "Die Beziehungen zwischen Farbe und Konstitution bei Farbstoffe," Zurich, 1921, p. 89.

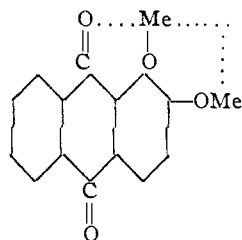
the color of alizarin (Formula IV) and other hydroxy-anthraquinone salts. He assumes that the formation of an *ortho*-quinoid ring which is favored by the influence of the hydroxy group in Position 1, produces red or blue colors (Formula V); and that the formation of a *para*-quinoid ring which may be attributed to the predominating influence of the hydroxy group in Position 2, produces yellow or brown colors. In a somewhat similar fashion, Scholl and Zinke<sup>8</sup> and O. Baudisch<sup>9</sup> describe the salts and lakes of alizarin and other hydroxy-anthraquinones as inner complex compounds in which the partial valences indicated by dotted lines are variable in their values. (Formula VI).



Alizarin  
(orange-red)  
IV



Salts of Alizarin  
(purple-blue)  
V



VI

The theory of Georgevics was criticised by Meek and Watson<sup>10</sup> because, as they stated, it was not entirely in harmony with the facts. They suggested the following generalizations which they claim are applicable not only to polyhydroxy-anthraquinone, but to other classes of dyes.

"(a) Two hydroxyl groups in one benzene nucleus in the *ortho* or *para* position with respect to one another are necessary to produce a deep (red, violet, or blue) color.

(b) The color is still further deepened if both benzene nuclei contain pairs of hydroxyl groups in the *o*- or *p*- position to one another.

(c) Three hydroxyl groups in the 1:2:4 positions in one benzene nucleus produce a deeper color than a pair of hydroxyl groups in the *o*- and *p*- positions.

(d) Three hydroxyl groups in the 1:2:3 positions in one benzene nucleus produce a brown color."

It is the opinion of the present writers that the correct explanation for the colors of the hydroxylamine derivative of anthraquinone and its salt will not be definitely established until the investigation is carried considerably beyond the scope of the present work.

### Properties of Pure 1-Nitro-anthraquinone

Since 1-hydroxylamino-anthraquinone has no definite melting point by which its degree of purity may be checked, and since it is very difficult to purify it by the usual methods of crystallization, it became obvious that

<sup>8</sup> Scholl and Zinke, *Ber.*, **51**, 1419 (1918).

<sup>9</sup> Baudisch, *ibid.*, **52**, 146 (1919).

<sup>10</sup> Meek and Watson, *J. Chem. Soc.*, **109**, 557 (1916). "Colour in Relation to Chemical Constitution," E. R. Watson, Longmans, Green and Co., 1921, p. 101.

the 1-nitro-anthraquinone used in this investigation should be as pure as possible. There are many methods of preparation given in the literature,<sup>11</sup> most of which depend on the action of strong nitric acid (sp. gr. 1.4–1.5), or "mixed acids" on anthraquinone. Most of these methods were tried in this laboratory and found unsatisfactory for the preparation of pure 1-nitro-anthraquinone. They invariably produced mixtures of unchanged anthraquinone, 1-nitro-anthraquinone and dinitro-anthraquinone, which were exceedingly difficult to separate completely by any method at our disposal.

In this connection, it is interesting to note that the melting point of pure 1-nitro-anthraquinone was in dispute during the years 1882–1897. Boettger and Peterson, in 1873, prepared it by heating anthraquinone with conc. nitric acid (sp. gr. 1.48–1.50). They found the melting point to be 230°. On reduction with sodium hydrogen sulfide, it gave an amine which melted at 256°. In 1882, Roemer, by treating anthraquinone with a mixture of nitric acid and sulfuric acid, obtained a 1-nitro compound melting at 220° which he thought to be different from that obtained by Boettger and Peterson because of the difference in melting points. Graebe and Liebermann<sup>12</sup> cleared up the confusion by proving that both compounds were identical because they gave the same amine which melted, after purification, at 242–243° (corr.). They also found that the corrected melting point of 1-nitro-anthraquinone was 228°. However, there still seems to be some question concerning the true melting point of 1-nitro-anthraquinone, since Barnett in his recent book on "Anthracene and Anthraquinone"<sup>11</sup> uses the melting point found by Roemer, namely, 220°.

In order to avoid further confusion from this source, we have determined the melting points of 1-nitro-anthraquinone and the amino derivative, after obtaining both of these compounds in a high state of purity. Our values for these compounds are higher than those given by Graebe and Liebermann, namely, 1-nitro anthraquinone, 232.5–233.5° (corr.), and 1-amino-anthraquinone, 252–253°(corr.).<sup>13</sup> The lower melting points usually found for 1-nitro-anthraquinone are undoubtedly explained by the difficulty of separating it from impurities. On the other hand, amino-anthraquinone is remarkable for the fact that its melting point seems to

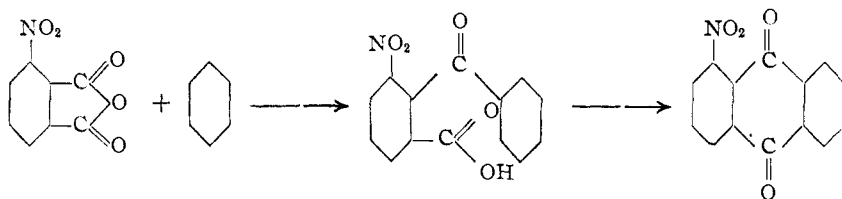
<sup>11</sup> Boettger and Peterson, *Ann.*, **166**, 147 (1873). Claus and Hertel, *Ber.*, **14**, 977 (1881). Roemer, *ibid.*, **15**, 1787 (1882). Liebermann, *ibid.*, **16**, 54 (1883). Müller, *Z. Elektrochem.*, **7**, 797 (1901). Lauth, *Compt. rend.*, **137**, 661 (1903). Ullmann and von der Schalls, *Ann.*, **388**, 203 (1912). Barnett, "Anthracene and Anthraquinone," D. Van Nostrand Co., 1922, p. 167.

<sup>12</sup> Graebe and Liebermann, *Ber.*, **30**, 1117 (1897).

<sup>13</sup> The corrected melting points were determined with a short-stem thermometer with the mercury column completely immersed in the bath. The melting points, as found by the usual method (using a long-stem thermometer) were as follows: 1-nitro-anthraquinone, 226–227°; 1-amino-anthraquinone, 245–246°.

be very little affected by the impurities formed when an impure sample of nitro-anthraquinone is reduced. A sample of very impure 1-nitro-anthraquinone melting at 190–220° on reduction with sodium sulfide gave a crude amine which melted at 243–245° and, therefore, led us to believe that it was practically pure. However, when the amine was recrystallized, we found that it contained a large amount of unchanged anthraquinone and probably some diamines.

The phthalic acid synthesis, which may be used for preparing anthraquinone, many of its homologs and certain of its derivatives, does not seem to be applicable for the preparation of 1-nitro-anthraquinone. It might be expected that 1-nitro-phthalic anhydride would condense with benzene in the presence of aluminum chloride to give a nitrobenzoyl-benzoic acid which, on treatment with dehydrating agents, would form 1-nitro-anthraquinone, just as phthalic acid and benzene react to give benzoyl-benzoic acid from which anthraquinone is obtained without difficulty.



All attempts to bring about this synthesis by the usual methods failed completely. The condensation product was always dark colored material, which could not be purified or converted into 1-nitro-anthraquinone.

A study of the reaction between 1-nitro-phthalic anhydride and benzene in the presence of aluminum chloride was made recently by Lawrance.<sup>14</sup> He succeeded in isolating the two possible condensation products, 2-benzoyl-3-nitrobenzoic acid and 2-nitro-6-benzoylbenzoic acid, but the yields were very poor (about 10% of the amount calculated) and 55–60% of the anhydride was recovered unchanged. Apparently no attempt was made by Lawrance to close the ring so as to form nitro-anthraquinone.

Practically all of the 1-nitro-anthraquinone used in our work was prepared by a method devised in this laboratory after considerable experimental work. It consists in heating anthraquinone with fuming nitric acid (sp. gr. 1.60) and crystallizing the crude product successively from glacial acetic acid, from toluene and, finally, from acetone. This method produces a very pure product. The details are given in the experimental part.

#### Conversion of 1-Nitro-anthraquinone into 1-Hydroxylamino-anthraquinone

The methods of Schmidt and Gattermann (with sodium stannite)

<sup>14</sup> Lawrance, *THIS JOURNAL*, **42**, 1871 (1920).

and of Wacker (with glucose and sodium hydroxide) for the reduction of 1-nitro-anthraquinone to the hydroxylamine derivative are difficult to carry out successfully. The conditions under which these reactions proceed, namely, in the presence of a warm solution of an alkali, are quite favorable to further reduction to the amine. We found that reduction is best brought about by the action of hydrogen sulfide upon a suspension of the nitro compound in pyridine at 0°. Under these conditions there is very little, if any, tendency for further reduction to the amine. The hydroxylamine derivative separated as a dark colored powder which crystallized from chloroform in the form of small maroon colored needles, and from methanol in clusters of the same color.

For the sake of comparison and contrast with the results of the present work, some of the characteristic properties of  $\beta$ -phenylhydroxylamine may be mentioned. It is a colorless solid melting at 81°. In its chemical properties it plays the dual role of a reducing agent and an oxidizing agent. Chromic acid readily oxidizes it to nitrosobenzene. It reduces Fehling's solution and an ammoniacal solution of silver nitrate. Furthermore, in the presence of an alkali it absorbs oxygen from the air and is converted into various products, among them nitrobenzene accompanied by some hydrogen peroxide. Even a neutral solution of it in water takes up oxygen from the air; nitroso-benzene and an equivalent amount of hydrogen peroxide are the primary products. In the absence of air, an alkaline solution undergoes intramolecular oxidation and reduction, and nitrosobenzene and aniline are formed primarily. It condenses, even at room temperature, with benzaldehyde to form a N-substituted aldoxime.<sup>15</sup> When hydrogen chloride is passed through its solution in ether,  $\beta$ -phenylhydroxylamine hydrochloride separates as colorless crystals. A solution of sodium nitrite at 0° converts the hydrochloride to  $\beta$ -phenylnitroso-hydroxylamine.<sup>16</sup> It reacts with diazo-benzene to form phenyl-diazo-hydroxylaminobenzene.<sup>17</sup>

Unlike  $\beta$ -phenylhydroxylamine, which is a colorless solid with a definite melting point, 1-hydroxylamino-anthraquinone crystallizes in dark maroon colored crystals, which decompose without showing a definite melting point. The group,  $-NHOH$ , acts, in this case, as an auxochromic group; a distinct change in color from anthraquinone itself results from its substitution. Furthermore, when this compound is converted into its sulfonic acid derivative, it dyes wool and silk without a mordant, producing shades of red-brown which are comparatively stable to light. A sample of wool dyed with this material showed no change after being exposed to the sun for 2 weeks. One of the most striking properties of this hydroxylamine

<sup>15</sup> Bamberger, *Ber.*, 27, 1556 (1894).

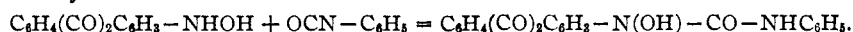
<sup>16</sup> Ref. 15, p. 1553.

<sup>17</sup> Ref. 3, p. 1434. Bamberger, *Ber.*, 29, 102 (1896).

derivative is the pronounced change in color which results when it is treated with alkalis; deep blue-green solutions are formed from which the original material may be precipitated by the addition of acid,—provided the alkaline solution is not exposed too long to the air. If air is passed through the alkaline solution, 1-nitroso-anthraquinone is precipitated and some hydrogen peroxide is formed.

The potassium salt of 1-hydroxylamino-anthraquinone was isolated by adding the calculated amount of potassium ethylate to an acetone solution at 0°. It proved to be a very unstable substance; it is oxidized on exposure to the air. When it was washed with ether in a suction funnel, sufficient heat was generated to cause a considerable amount of the ether to vaporize. The salt, when freshly prepared is dark green in color, and it dissolves with some difficulty in warm water, but more readily in a mixture of acetone and water to give the characteristic blue-green solution. After exposure to air for some time, it becomes red-brown in color because of oxidation to the nitroso compound which may be extracted from the residue.

The hydroxylamine derivative is a fairly strong reducing agent, since it reduces an ammoniacal solution of silver nitrate almost instantly in the cold, but it has very little effect on Fehling's solution. It forms a substituted urea derivative when it is boiled with a solution of phenyl-isocyanate in dry toluene.



The hydroxylamine derivative is remarkably stable toward aldehydes. It does not combine with acetaldehyde even when the mixture is heated in a sealed tube at 100°. It may be dissolved in boiling benzaldehyde and crystallized from it without undergoing any change. It shows some base-forming properties, since it dissolves in strong acids, but no hydrochloride could be isolated by the usual method. When it was treated with nitrous acid in the presence of a mineral acid, no nitroso-hydroxylamine could be isolated, although  $\beta$ -phenylhydroxylamine undergoes this reaction readily. It reacts with benzoyl chloride or with acetyl chloride in alkaline solution, presumably to form the benzoyl or the acetyl derivative. We were unable to isolate a pure material in either case, so the products were not analyzed. When diazobenzene reacts with the hydroxylamine derivative in alkaline solution, the blue-green color is destroyed and a red-brown powder is formed which melts with decomposition at about 140°. We were unable to find a suitable solvent for purifying this material, so it was not analyzed.

### Experimental Part

#### The Preparation of Anthraquinone from Anthracene by Sulfuric Acid and Sodium Dichromate

In order to prepare pure 1-nitro-anthraquinone by the method described, it is necessary to employ a good grade of anthraquinone. The usual laboratory method for

oxidizing anthracene to anthraquinone consists in treating anthracene in glacial acetic acid with chromic acid. We have found that the commercial method, which employs sulfuric acid and sodium dichromate in water solution, when properly applied, gave a better yield and was generally more satisfactory. This method is a modification of the method taken from patent literature and given by Weyl.<sup>18</sup>

Seventy-five g. of anthracene (m. p. 205–209°) was suspended in 300 cc. of boiling water in a 2-liter beaker. It is necessary to use a fairly large container and an efficient mechanical stirring device to prevent loss from foaming. To this mixture was added a solution of 180 g. of technical sodium dichromate dissolved in a small amount of hot water. While the solution boiled and was stirred rapidly, a mixture of 225 g. of conc. sulfuric acid and 150 g. of water was added through a funnel drop by drop. After all the acid had been introduced, the mixture was boiled and stirred for about 1 hour. The product was allowed to cool partially, and was filtered with the aid of a pump. The precipitate was washed with boiling water until it was free from chromium salts. The crude product melted at 274–276°; yield, 98%. It was dissolved in three times its weight of aniline, from which it crystallized in the form of light yellow needles. This material was collected on glass wool in a Hirsch funnel, washed first with a little aniline, and then the aniline was removed with methyl alcohol. Yield, 80–85%; m. p., 277–278°.

NOTES.—1. Excessive foaming, which sometimes takes place, may be overcome if the flame is removed and the flow of acid is stopped for a moment. If this fails, a little cold water from a wash bottle should be poured down the inside of the beaker.

2. Anthraquinone separates from aniline as a semi-solid mass which should be broken up with a glass rod to form a thin paste.

3. The crude anthraquinone as obtained above may be purified further by heating it with 100% sulfuric acid at 120° for 2 hours. This solution, still hot (80–90°), is poured into a large volume of boiling water, and the precipitated anthraquinone is collected. The precipitate should be washed with hot water, then with a hot dil. solution of sodium hydroxide and, finally, with hot water. It is very light gray in color. It crystallizes from chloroform in silky, hair-like crystals almost white in color. The yield and melting point are practically the same as before.

#### The Preparation of Pure 1-Nitro-anthraquinone

Thirty-five g. of finely powdered anthraquinone was suspended in 280 g. of fuming nitric acid (sp. gr. 1.60) in a 500cc. flask. The mixture was boiled gently on a water-bath for exactly 40 minutes; during this time it was shaken occasionally to insure complete solution. The initial temperature of the water-bath was 55°; it was gradually increased to 70–75°. When the solution had cooled partially, it was poured slowly into about 3 liters of cold water which was stirred. The nitro-anthraquinone was washed several times by decantation, collected and washed thoroughly with boiling water. Yield, 40 g.; m. p. 190–225°. This crude product was refluxed with 800 cc. of glacial acetic acid and filtered from insoluble matter. Most of the 1-nitro compound separated as the solution cooled. Yield, 25–30 g.; m. p., 215–220°. It was crystallized from 700 cc. of toluene. Yield, 20–25 g.; m. p., 220–222°. This product was finally crystallized from about 1200 cc. of acetone, from which it separated in large, brilliant, amber-colored, tetragonal prisms. Yield, 15–18 g. (about 40%); m. p. 226–227°; m. p. (corr.), 232.5–233.5°.

*Analysis.*<sup>19</sup> Subs., 0.4093: N, 20.8 cc. (26°, 766 mm.). Calc.: N, 5.54 Found: 5.67

<sup>18</sup> Weyl, "Die Methoden der Organischen Chemie," vol. 2, p. 962. References to the patent literature are given here also.

<sup>19</sup> The nitrogen in each case was collected over KOH solution made by dissolving 30 g. of KOH in 100 cc. of water.



**1-Amino-anthraquinone, by the Reduction of the Nitro Compound<sup>20</sup>**

Two g. of this pure sample of 1-nitro-anthraquinone was ground in a mortar with 4 g. of potassium sulfide and sufficient water to make a thin paste. This paste, which was dark green in color, was poured into 200 cc. of boiling water, and the mixture was boiled for about 1 hour. The amino compound was collected and washed thoroughly with boiling water. It was a brick-red powder, with a bronze-like luster. It crystallized from absolute alcohol in beautiful, long, bright red needles with a distinct greenish sheen. Yield, 2 g.; m. p., 245-246°; m. p., (corr.) 252-253°.

*Analysis.* Subs., 0.3575: N, 19.6 cc. (18°, 756 mm.). Calc.: N, 6.28. Found: 6.29.

**1-Hydroxylamino-anthraquinone, by the Reduction of the Nitro Compound with Pyridine and Hydrogen Sulfide**

Two hundred cc. of pyridine (technical) was placed in a 500cc. Erlenmeyer flask and saturated with dry hydrogen sulfide at 0°. To the ice-cold solution, 8 g. of very finely powdered 1-nitro-anthraquinone was added in small portions while the flask was shaken vigorously. The nitro compound dissolved quite readily, and was reduced to the hydroxylamino compound which formed a solution intensely red in color. After all of the nitro compound except a slight residue was dissolved, the solution was poured into about 2 liters of cold water which was stirred to complete the precipitation. The hydroxylamino derivative separated as a dark maroon colored precipitate. It was collected rapidly and washed with hot water to remove pyridine. The precipitate was transferred to a 700cc. flask and suspended in a mixture of 100 cc. of acetone and 300 cc. of water at 40-60°. Forty cc. of a 1:3 solution of sodium hydroxide was added and the flask was shaken vigorously for a few moments to dissolve the hydroxylamine as the sodium salt. The presence of the acetone in this mixture greatly facilitates the transformation to the sodium salt, and prevents any appreciable oxidation by the air. The blue-green solution was filtered immediately through hardened filter paper into a mixture of 750 cc. of water and 40 cc. of conc. hydrochloric acid. The hydroxylamine derivative was collected and washed with boiling water; yield, 7 g. It was crystallized from methanol in the form of maroon colored clusters. Yield, 6.5 g.

*Analysis.* Subs., 0.3730: N, 19.6 cc. (22°, 758 mm.). Calc.: N, 5.87. Found: 5.91.

It is soluble in most of the ordinary organic solvents, especially in hot acetone and in hot or cold pyridine.

**The Potassium Salt of the Hydroxylamine Derivative**

One g. of the hydroxylamine derivative was dissolved in a small amount of acetone. The solution was cooled with ice and treated with the calculated amount of potassium ethylate. The color of the solution gradually changed from red-brown to dark-green and a precipitate formed. Ether was added to precipitate the salt completely, which was then collected on a filter and washed with ether. While the ether was being removed by suction, considerable heat was evolved as a result of the action of oxygen on the salt. The salt was dark green when wet, and became red-brown when dry, yield, about 1.2 g. It was soluble with difficulty in warm water, and more readily in acetone and water forming the characteristic deep blue-green solution. After exposure of the solid salt to the air for 4 days, no blue-green color was apparent when it was treated with water, or a mixture of acetone and water.

The remaining material, which was red-brown in color, was washed with hot water to remove any alkali. A sample of the residue crystallized from alcohol in the form

<sup>20</sup> Barnett, Ref. 11, p. 192.

of old-rose colored needles which melted at 219–221°. This melting point is several degrees lower than the true melting point of 1-nitroso-anthraquinone (*See following preparation*). It was not purified further because the sample was too small. It gave Liebermann's test for nitroso compounds. When treated with hydrogen sulfide in pyridine solution, it was reconverted to the hydroxylamine derivative.

#### 1-Nitroso-anthraquinone, by the Oxidation of the Hydroxylamine Derivative with Air

Two g. of the hydroxylamine derivative was dissolved in about 400 cc. of water and 35 cc. of a 1:3 solution of sodium hydroxide. The solution was filtered to remove any insoluble material. A rapid current of air, free from carbon dioxide, was passed through the filtrate. The color of the filtrate changed gradually from deep blue-green to dark red, and a precipitate formed. After no further change took place (3–4 hours), the air stream was stopped and the precipitate was collected. It was a red powder with a violet tinge. It crystallized readily from alcohol, from benzene, from toluene, and from chloroform. It gave Liebermann's nitroso reaction when treated with phenol and conc. sulfuric acid. It was reduced to the hydroxylamine derivative by treatment with potassium sulfide or hydrogen sulfide and pyridine. From alcohol, it separated in old-rose colored needles which melted at 223–224°; yield, 1 g.

*Analysis.* Subs., 0.1915: N, 10 cc. (26°, 763 mm.). Calc.: N, 5.95. Found: 5.80.

Hydrogen peroxide was detected in the filtrate separated from the nitroso compound, by the action of a dil. solution of potassium dichromate upon a portion of it acidified with dil. sulfuric acid and covered with ether. The characteristic blue color was produced in the ether layer. The presence of hydrogen peroxide was confirmed also by shaking some of the filtrate with benzoyl chloride until white crystals separated. When these crystals were brought in contact with an acid solution of potassium iodide containing some starch, iodine was liberated abundantly. This is characteristic of benzoic peroxide.

#### The Substituted Urea Derivative

One g. of finely powdered hydroxylamine derivative was suspended in about 100 g. of dry, freshly distilled toluene containing 0.8 g. of phenyl isocyanate. (*See p. 2302.*) The mixture was refluxed for about 3 hours. The hot solution was filtered to separate a small amount of insoluble matter and, as it cooled, fairly long, dark red-brown needles formed on the walls of the flask. Yield, 0.6 g. Melting point, 236°.

*Analysis.* Subs., 0.3000: N, 22.2 cc. (23°, 761 mm.). Calc.: N, 7.9. Found: 8.3.

**Hydrolysis of the Substituted Urea.**—One g. of the urea derivative was heated in a sealed tube for 3 hours at 200° with about 50 cc. of conc. hydrochloric acid. When the tube was opened, the gas which escaped produced a white precipitate with baryta water; this proved the presence of carbon dioxide. The hydrochloric acid solution was red-brown in color. It was made alkaline with sodium hydroxide and distilled with steam. The distillate showed the presence of aniline; it gave a dark violet color with a solution of bleaching powder, a red-brown (nearly black) color with sulfuric acid and potassium dichromate, and a white precipitate with bromine water. This white precipitate was identified as *sym*-tribromo-aniline by crystallizing it from alcohol and determining its melting point, which was found to be 118–119°.

#### Summary

1. New methods for preparing 1-nitro-anthraquinone and 1-hydroxy-1-amino-anthraquinone have been devised.

2. The melting points of pure 1-nitro-anthraquinone and of pure 1-amino-anthraquinone were found to be considerably higher than the values given in the literature.

3. The properties and reactions of 1-hydroxylamino-anthraquinone are described.

PRINCETON, NEW JERSEY

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF NEBRASKA]

## THE DECOMPOSITION OF AMINES IN THE VAPOR STAGE

BY FRED W. UPSON AND LILA SANDS<sup>1</sup>

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This paper presents the results of experiments on the decomposition of amines in the vapor stage in the presence of kaolin.

### Experimental

**Description of the Apparatus.**—The reaction chamber consisted of a silica tube drawn out to a capillary of about 1 mm. internal diameter at one end, heated in an electric furnace controllable within a range of 10°. Temperature readings were made by means of a base-metal thermocouple and a millivolt meter. The tube was packed with kaolin in pieces about 18 mm. long and 3 mm. in diameter.

The sample of amine was contained in a sealed tube, with a side arm carrying a glass stopcock, by means of which union with the capillary of the silica tube was made. The products of decomposition on leaving the tube passed first through a U-tube surrounded by a freezing mixture, then through a wash-bottle containing standard acid, and finally gaseous products were collected in a container over mercury. Connections were of sealed glass wherever possible. By means of a side tube fitted with glass stopcocks the whole apparatus could be evacuated to about 4 mm. pressure. The sample of amine was admitted to the reaction tube by opening the stopcock on the side-arm tube, the last traces being expelled by gentle heating.

**Ethyl Amine.**—The decomposition of ethyl amine was carried out at three different temperatures, 500°, 700° and 1000°. Except at the highest temperature, gaseous, liquid and solid products appeared. The gaseous products consisted of saturated and unsaturated hydrocarbons, nitrogen and hydrogen. In the analysis of the gas mixture unsaturated hydrocarbons were absorbed in bromine water; hydrogen and saturated hydrocarbons were determined by burning in a combustion pipet. Hydrogen was determined in a separate sample by burning over palladium black at 60°.

<sup>1</sup> The results here presented have been embodied in a dissertation for the Master's degree by Lila Sands.