[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY]

DINITROSO-RESORCINOL[1]

BY W. R. ORNDORFF AND M. L. NICHOLS

Received February 17, 1923

Dinitroso-resorcinol is first mentioned by Fitz,[2] who obtained it by the action of potassium nitrite upon resorcinol in acetic acid solution at a temperature of about 0°.

He states that it was impossible to determine the water of crystallization directly as there was only a slight loss in weight at 100°, and at 115° the dinitroso-resorcinol explodes. However, he gives analyses to show that the dinitroso-resorcinol contains 2 molecules of water of crystallization.

From the results of their investigation on the structure of the nitroso derivatives of the polyacid phenols, Goldschmidt and Strauss[3] believed that dinitroso-resorcinol possesses the symmetrical oxime structure. Kostanecki,[4] however, from his investigation of the nitroso derivatives of orcinol and β-orcinol came to the conclusion that dinitroso-resorcinol has the unsymmetrical oxime structure (see formula below). The correctness of this opinion was proved by the investigation of the behavior of cresorcinol with nitrous acid. Further evidence of this structure for dinitroso-resorcinol was obtained by Liebermann and Kostanecki[5] who found that unsymmetrical phenyldisazo-resorcinol is reduced to the same diamino-resorcinol that Fitz obtained by reducing dinitroso-resorcinol. This same diamino-resorcinol was also secured by Harpe and Reverdin[6] by the reduction of nitroso-nitroresorcinol which possesses the adjacent structure. Kostanecki[7] then tried to obtain an isomeric symmetrical dinitroso-resorcinol by the action of nitrous acid on mononitroso-resorcinol but he obtained only the ordinary unsymmetrical dinitroso-resorcinol, which according to his analyses contains only 1 molecule of water of crystallization. He also obtained the same results with some dinitroso-resorcinol prepared according to the method of Fitz. From his investigation of dinitroso-resorcinol in 1903, Bulow[8] states that it contains only 0.5 molecule of water of crystallization and that it decomposes at 163–166°. Later Barberio[9] worked with dinitroso-resorcinol and confirmed the results given by Fitz.

So far, symmetrical diamino-resorcinol has been prepared by Typke,[10] Kostanecki,[11] Nietzke and Schmidt[12] and Kehrmann and Betsch[13] but never from dinitroso-resorcinol, which, with all of the previously mentioned

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[1] From a dissertation presented by M. L. Nichols in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Fitz, *Ber.*, **8**, 631 (1875).

[3] Goldschmidt and Strauss, *ibid.*, **20**, 1607 (1887).

[4] Kostanecki, *ibid.*, **20**, 3133 (1887).

[5] Liebermann and Kostanecki, *ibid.*, **17**, 876 (1884).

[6] Harpe and Reverdin, *ibid.*, **21**, 1405 (1888).

[7] Kostanecki, *ibid.*, **22**, 1345 (1889).

[8] Bulow, *ibid.*, **36**, 730 (1903); **37**, 1791 (1904).

[9] Barberio, *Gazz. chim. ital.*, [2] **37**, 579 (1907).

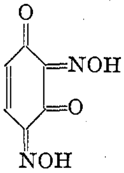
[10] Typke, *Ber.*, **16**, 551 (1883).

[11] Kostanecki, *ibid.*, **21**, 3114 (1888).

[12] Nietzke and Schmidt, *ibid.*, **22**, 1653 (1889).

[13] Kehrmann and Betsch, *ibid.*, **30**, 2096 (1897).

work on this substance, shows conclusively that dinitroso-resorcinol possesses the adjacent oxime structure.



Dinitroso-resorcinol

It will be seen from this brief review of the literature that there is some doubt as to the composition of dinitroso-resorcinol. Fitz and Barberio give its formula as $C_6H_2O_2(NOH)_2.2H_2O$ and decomposition point as 115°, Kostanecki as $C_6H_2O_2(NOH)_2.H_2O$ and Bulow as $C_6H_2O_2(NOH)_2.0.5H_2O$, while Bulow gives its decomposition point as 163–166°. As it was desired to use dinitroso-resorcinol to determine cobalt it was necessary to prepare the substance in the pure state and to determine its composition and decomposition point.

Experimental Part

The resorcinol used in the preparation of the dinitroso-resorcinol was distilled in a partial vacuum[14] giving a pure white product melting at 109.5° to a clear, colorless liquid.[15] The decomposition point of dinitroso-resorcinol given in this paper is uncorrected and was determined in an electrically heated, Dennis melting-point apparatus,[16] the heat being regulated so as to give a rise in temperature of 1° in 7 seconds and much slower through the last 10°.[17] The thermometer used was calibrated against a standard thermometer. Samples for analysis were dried to constant weight in a vacuum desiccator over concd. sulfuric acid. An electrically heated tube[18] was used to determine the loss in weight of the substance on drying at a constant temperature. A narrow strip of asbestos board was placed in the bottom of the tube to prevent the superheating of the bottom of the boat. All nitrogen determinations were made by the Kjeldahl method by first reducing the dinitroso-resorcinol with zinc dust and dil. sulfuric acid. All combustion analyses were made by the usual method for compounds containing nitrogen. The values used for the atomic weights are those given in the 1922 International Table of Atomic Weights.[19]

The dinitroso-resorcinol was prepared from resorcinol by the following method, which is a modification of that used by Fitz.

[14] Gattermann, "Practical Methods of Organic Chemistry," Macmillan Co., **1916**, p. 26.

[15] P. Lemaire, *Bull. soc. pharm.* (*Bordeaux*), **50,** p. 110.

[16] Dennis, *J. Ind. Eng. Chem.*, **12,** 366 (1920).

[17] Wegscheider, *Chem.-Ztg.*, **29,** 1224 (1905).

[18] Orndorff and E. H. Nichols, *Am. Chem. J.*, **48,** 477 (1912).

[19] THIS JOURNAL, **44,** 427 (1922).

To a solution of 20 g. of resorcinol (1 molecule) in a liter of water 21.8 g. of glacial acetic acid (2 molecules) was added. The solution was placed in a 2-liter beaker, surrounded by a freezing mixture, and stirred rapidly with a mechanical stirrer until the temperature had fallen slightly below 0°. While rapid stirring was continued, a standard solution of sodium nitrite (0.1604 g. per cc.) was slowly added from a buret. The total of sodium nitrite solution used, 150 cc., was added in about 40 minutes, and the temperature of the solution was not allowed to rise above 0°. A much lighter colored product is secured when the temperature is not allowed to rise above 0° and slightly less than the theoretical amount of sodium nitrite (2 molecules) is used. After the addition of the sodium nitrite the stirring was continued for about 15 minutes and then the entire mass was poured into 35.9 g. of sulfuric acid (2 molecules), diluted to 1 liter and cooled to about 10°. The mixture was stirred for about 10 minutes and then the free dinitroso-resorcinol was allowed to settle. After about one hour it was separated on a Büchner funnel, washed thoroughly with cold water and allowed to dry in the air; yield, 32 g., or 94.6%. Working in an atmosphere of carbon dioxide and using water saturated with carbon dioxide do not have an appreciable effect upon the color of the final product. The dinitroso-resorcinol was recrystallized from 50% alcohol, by heating the latter almost to boiling in a beaker and adding dinitroso-resorcinol until there was a slight excess which would not dissolve, filtering the solution rapidly through a hot-water funnel, and letting it cool slowly, with stirring. The crystalline dinitroso-resorcinol was filtered off and washed thoroughly with water, which gave a product of light yellowish-brown, glistening leaflets.

The crystals of dinitroso-resorcinol were examined by Professor A. C. Gill of the Mineralogical Department of Cornell University, who reports as follows, "This substance crystallizes in very thin rhombic plates. Frequent occurrence of triangular forms suggests the possibility, or probability even, of rhombic pyramidal symmetry. Hence, the setting of the crystals with the tabular face as the macropinacoid (100) was chosen.

"An approximate determination of the axial ratio gave a : b : c = 0.9(?) : 1 : 0.613.

"The most sharply defined edge of the thin crystals is parallel to (011) the brachydome or brachydomatic sphenoid. There is a very perfect basal cleavage, which may account for the hemimorphic appearance of the crystals, though there are more than would seem probable from this cause.

"The substance is strongly pleochroic from pale yellowish or greenish tints for light vibrating parallel to the vertical axis to tobacco-brown for the other two elasticity axes.

"The double refraction is extreme, approximately 0.450 (?). The plane of the optical axes is doubtless the macropinacoid. Interference colors and absorption indicate a negative character with the vertical (c) axis as acute bisectrix. The corresponding index of refraction is very near 1.44."

The dinitroso-resorcinol was dried to constant weight in a vacuum desiccator over sulfuric acid. It lost most of the water in the first 6 days but required 40 days to come to constant weight, and the loss was 0.815%.

Contrary to the statement of Fitz, it was found that the water of crystallization could be determined by drying the substance to constant weight at 105° in an atmosphere of carbon dioxide. The following results were obtained on the product dried to constant weight over sulfuric acid in a vacuum desiccator, as compared with results on material dried at 105°.

Subs. (vacuum-dried), 0.6822, 0.6625, 0.6094, 0.6604, 0.5982, 0.7131: H_2O, 0.0662, 0.0637, 0.0594, 0.0646, 0.0577, 0.0689. Calc. for $C_6H_2O_2(NOH)_2.H_2O$: 9.68. Found: 9.70, 9.62, 9.75, 9.78, 9.65, 9.66; av. 9.69.

Subs. (vacuum-dried), 0.4972, 0.4972: 53.45, 53.38 cc. of 0.1 *N* H_2SO_4. Calc. for $C_6H_2O_2(NOH)_2.H_2O$: N, 15.06. Found: 15.06, 15.04.

Subs. (dried at 105°), 0.4304, 0.5958: 50.84, 70.28 cc. of 0.1 *N* H_2SO_4. Calc. for $C_6H_2O_2(NOH)_2$: N, 16.67. Found: 16.55, 16.53.

Subs. (vacuum-dried), 0.2054, 0.2194: CO_2, 0.2933, 0.3118; H_2O, 0.0622, 0.0675. Calc. for $C_6H_2O_2(NOH)_2.H_2O$: C, 38.71; H, 3.25. Found: C, 38.95, 38.77; H, 3.40, 3.44.

The decomposition point of the dinitroso-resorcinol was found to be 162–163°, and not 115°.

In addition to the solubility in the various solvents mentioned by Fitz, it was found that dinitroso-resorcinol is insoluble in toluene, carbon tetrachloride or petroleum ether in the cold and very slightly soluble in these solvents at the boiling point. It is very slightly soluble in chloroform. An aqueous solution of the above dinitroso-resorcinol also gave the characteristic green color with ferric chloride solution, described by Fitz.

Summary

1. A method has been given for the preparation, purification and crystallization of dinitroso-resorcinol.

2. Dinitroso-resorcinol, when dried to constant weight in a vacuum desiccator over sulfuric acid, contains 1 molecule of water of crystallization and has the composition indicated by the formula $C_6H_2O_2(NOH)_2.H_2O$.

3. Pure crystalline dinitroso-resorcinol decomposes at 162–163° instead of at 115° as is almost always stated.

4. The action of several solvents upon dinitroso-resorcinol has been studied.

5. The crystal form and characteristics of dinitroso-resorcinol have been determined.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, THE ROOSEVELT HOSPITAL]

STUDIES ON ENZYME ACTION. XXIII. THE SPONTANEOUS INCREASE IN SUCRASE ACTIVITY OF BANANA EXTRACTS

BY GRACE MCGUIRE AND K. GEORGE FALK

Received February 19, 1923

Introduction

The enzymic hydrolysis of sucrose has been investigated to a greater extent probably than any other enzyme action. Reference may be made especially to the pioneering work of O'Sullivan and Tompson, and to the more recent extensive studies of Sörensen, Euler, Hudson, Michaelis, Nelson, and Willstätter, and their co-workers. These studies were concerned practically entirely with the sucrase obtained from yeast, sucrase from other sources being considered only incidentally. It seemed, therefore, to be of some interest to study more intensively the sucrase from a