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The Decomposition of 2,5-Dinitrobenzoic Acid by Alkali

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In attempts to explain the color given by 2,5-dinitrobenzoic acid in alkaline solution the effect of alkali alone upon the dinitro acid was studied.

Pure 2,5-dinitrobenzoic acid (m. p. 177–178°) in sodium bicarbonate solution is yellow and may be boiled with but slight intensification of color. In strong alkali (0.4 *N* sodium hydroxide), however, even at room temperature, intensification of color to deep red occurs over several weeks. The deep color develops quickly when the solution is heated. After one hour of heating, followed by acidification with hydrochloric acid, 2-hydroxy-5-nitrobenzoic acid, 5-hydroxy-2-nitrobenzoic acid and a non-crystalline brown acid were isolated. Nitrous acid and ammonia also were present in small amounts. Neither unchanged 2,5-dinitrobenzoic acid nor 2,5-dihydroxybenzoic (gentisic) acid could be detected. That the colored acid was probably a mixture of azo and hydrazo compounds was indicated by the composition of the material, and by its close similarity to colored substances which were subsequently prepared by reduction of 2,5-dinitrobenzoic acid with glucose in sodium carbonate solution (not reported herein). At this alkalinity 2,5-dinitrobenzoic acid is not decomposed, and under the conditions used, aromatic nitro compounds in general give rise to azo dyes.

After heating 2-hydroxy-5-nitrobenzoic acid in 0.4 *N* sodium hydroxide for one hour, the unchanged acid was recovered in 60% yield, and no other product could be isolated. No deep color was formed. With similar heating in alkali, 5-hydroxy-2-nitrobenzoic acid was recovered unchanged in 50% yield, a very small amount of unidentifiable red material being formed. Tests with ferric chloride gave no blue color with these alkaline solutions, from which it is concluded that gentisic acid was not present. It is evident from these findings that the hydrolysis of 2,5-dinitrobenzoic acid by strong alkali leads to the ready replacement of either, but not of both, atoms of nitrogen from the dinitrobenzoate.

Experimental

Isolation of the Acids.—For a typical hydrolytic decomposition, 2.0 g. of 2,5-dinitrobenzoic acid was suspended in 50 ml. of water, and 0.8 g. of sodium bicarbonate was added. When the evolution of carbon dioxide had ceased, an equal volume of 0.8 *N* sodium hydroxide was added. This solution was refluxed for one hour, during which time it became deep red. It was cooled, was acidified to congo red with 10% hydrochloric acid and was chilled, whereupon 0.63 g. of brown material separated. The filtrate upon being evaporated to 50 ml. and filtered yielded 0.025 g. more of the brown product.

The 50 ml. was evaporated nearly to dryness, and sodium chloride and a small amount of 2-hydroxy-5-nitrobenzoic acid were filtered off. Addition of ethanol to the filtrate aided in removing more sodium chloride.

The sirupy concentrate was extracted repeatedly with about 50 ml. of boiling toluene, the water remaining being distilled off with toluene vapor. Upon cooling the toluene, crystals separated and were filtered off; by several repetitions of the process with the toluene filtrate a total of 0.35 g. of crystalline material was obtained. A negligible amount of dark colored oil insoluble in the toluene but readily soluble in butanol remained, together with a small amount of ammonium chloride. After recrystallization of the product from toluene (0.3 g. dissolved in 90 ml. of boiling toluene, from which 0.235 g. was recovered), it melted at 165–166°, which is the melting point of 5-hydroxy-2-nitrobenzoic acid. Equiv. wt. found, 92.7, 91.5; calculated for hydroxynitrobenzoic acid, 91.5. The *p*-nitrobenzyl ester was prepared and after recrystallization from ethanol melted at 200–202°. The corresponding ester prepared from 2-hydroxy-5-nitrobenzoic acid which was purchased, melted at 115°.

The 0.65 g. of brown precipitate obtained above was extracted three times with about 50-ml. portions of boiling toluene, from which, after cooling, separated 0.22 g. of crystalline material, m. p. 224–225°. Mixed with 2-hydroxy-5-nitrobenzoic acid, the melting point was unchanged. The residue insoluble in toluene was then extracted with boiling water, and was filtered. The slightly soluble brown material separated as an oil, and the filtrate, after chilling, yielded 0.15 g. more of 2-hydroxy-5-nitrobenzoic acid. This process of fractionation was repeated several times when separation of the products seemed to be complete. The air dried brown solid decomposed gradually from about 250 to 300°. It repeatedly came out of 20% ethanol or from dilute 1,4-dioxane as an oil. It was readily soluble in hot butyl or in benzyl alcohol, from which it was precipitated as brown powder by careful addition of toluene. This powder was soluble in sodium bicarbonate with evolution of carbon dioxide. Since it did not give intensification of color upon being heated in 0.4 *N* sodium hydroxide, unchanged 2,5-dinitrobenzoic acid was not present. Attempts were made to obtain crystalline esters, the amide, and copper, barium, and calcium salts, but oils were always obtained. Combustion of the brown acid showed that it contained 47.4% carbon and 2.8% hydrogen. Nitrogen values by the Elek and Sobotka modifications of the Kjeldahl process¹ indicated the substance to be a mixture, as did titration values attempted with the deeply colored solutions, but the analyses established that two atoms of nitrogen per carboxyl group were present. The data, together with the physical properties, suggested strongly that the colored material was a mixture of azo and hydrazo compounds. Extraction with ether removed enough of an oil component so that the residue could be crystallized from hot 50% ethanol. In polarized light three different crystal forms were detected. After filtering off the first crop of obviously impure crystals, a second homogeneous crop melted sharply at 262°, but the crystals were too small for indices of refraction to be determined.

Subsequent experimental work involved the synthesis of 2-nitroso-5-nitrobenzoic acid, and of 2-nitro-5-nitrosobenzoic acid. Both nitroso acids failed to react with the 2,5-aminonitrobenzoic acids even in the presence of rather vigorous dehydrating agents. Therefore synthesis of the desired azo compounds having known structures for comparison with the above colored acid is still to be accomplished.

For the synthesis of 2-nitroso-5-nitrobenzoic acid, 2-amino-5-nitrobenzoic acid was prepared through the following series of reactions described by Hewitt and Mitchell,²

(1) Elek and Sobotka, *This Journal*, **46**, 501 (1926).

(2) Hewitt and Mitchell, *J. Chem. Soc.*, **91**, pt. 2, 1258 (1907).

and by Green and Day³: 2-acetamido-5-nitrotoluene → 2-acetamido-5-nitrobenzoic acid → 2-amino-5-nitrobenzoic acid.

The 2-amino-5-nitrobenzoic acid was then oxidized with Caro's acid as follows:

2-Nitroso-5-nitrobenzoic Acid.—A solution containing 2.5 ml. of water and 10 ml. of sulfuric acid (sp. gr. 1.85) was cooled to 5°. To it was added 4.1 g. of 2-amino-5-nitrobenzoic acid, the mass being broken up with a glass rod. Then 10 ml. more of cold sulfuric acid was poured in, followed by 25 g. of powdered ammonium persulfate. When a uniform paste was obtained, 20 ml. of ice water was added, whereupon the aminonitrobenzoic acid dissolved. The solution was warmed to 40°, and was held at that temperature. A brown precipitate separated after thirty minutes. After one and one-half hours another 10 g. of ammonium persulfate was added, the solution now being allowed to come to room temperature and to stand overnight. Then 50 g. of cracked ice was added and after fifteen minutes the cold solution was filtered with gentle suction through hardened filter paper. The brown product was washed with ice water and, after being dried in warm air, weighed 3.61 g. No more product could be obtained by further diluting and chilling the filtrate. The unpurified acid was cream colored and melted with decomposition at 202°. For recrystallization 1 g. was dissolved in 20 ml. of 50% ethanol and was chilled, 0.40 g. being recovered.

Anal. Equiv. wt., 0.2770 g. subs. neutd. 14.73 ml. of 0.0957 *N* sodium hydroxide to phenolphthalein endpoint. Calcd. for C₇H₄O₅N₂: equiv. wt., 196. Found: equiv. wt. 196.6.

2-Nitro-5-nitrosobenzoic Acid.—For the synthesis of this acid a series of reactions corresponding to that given above was carried out: 3-aminotoluene → 3-acetamidotoluene → 3-acetamido-6-nitrotoluene → 3-acetamido-6-nitrobenzoic acid → 3-amino-6-nitrobenzoic acid. The 3-amino-6-nitrobenzoic acid was oxidized as has been

(3) Green and Day, *THIS JOURNAL*, **64**, 1167 (1942).

described under 2-nitroso-5-nitrobenzoic acid. The sulfate was less soluble than that of 2-amino-5-nitrobenzoic acid, and was oxidized in more dilute solution. The crude, light brown product was recrystallized from dilute ethanol as follows: 1 g. was dissolved in 5 ml. of hot 95% ethanol and 12 ml. of hot water was added. After rapid filtration and cooling of the filtrate, 0.88 g. of 2-nitro-5-nitrosobenzoic acid, m. p. 270–270.5°, was filtered off.

Anal. Equiv. wt., 0.1270 g. subs. neutd. 6.11 ml. of 0.1058 *N* NaOH; 0.1737 g. subs. neutd. 8.42 ml. of 0.1058 *N* NaOH. Calcd. for C₇H₄O₅N₂: equiv. wt., 196. Found: equiv. wt., 196.6, 194.9.

Evaporation of the filtrates from the recrystallization yielded about 50 mg. of the nitrosnitro acid, and further evaporation to about 25 ml. yielded a light colored oil, which soon crystallized and proved to be 2,5-dinitrobenzoic acid.

Summary

By alkaline hydrolysis of 2,5-dinitrobenzoic acid either nitro group may be replaced by hydroxyl, giving rise to 2-hydroxy-5-nitrobenzoic acid, and to 5-hydroxy-2-nitrobenzoic acid. Gentisic acid seemed not to be formed. A brown oil also was isolated. This was a mixture probably of azo and hydrazo compounds, which were not identified.

Synthesis of 2-nitroso-5-nitrobenzoic acid and of 2-nitro-5-nitrosobenzoic acid showed these substances to be practically colorless and unlike the colored product formed by the action of alkali upon 2,5-dinitrobenzoic acid. Both nitroso acids were non-reactive toward the 2,5-aminonitrobenzoic acids.

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[CONTRIBUTION FROM THE NAVAL RESEARCH LABORATORY]

Ultrasonic Investigation of Molecular Properties of Liquids. II.¹ The Alcohols^{1a}

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Although several investigators^{2,3,4,5} have measured the velocity of sound in a variety of liquids, the application of their data to chemical problems has been relatively neglected.⁶ Inasmuch as a sound wave is a mechanical impulse transmitted from molecule to molecule, one expects the properties of the molecule to affect the rate of transmission of this impulse.

The use of ultrasonic frequencies permits the apparatus to be of conveniently small size, yet

(1) Part I, Weisser, Fitzgerald, and Resnick, *J. Appl. Phys.*, **18**, 434 (1947).

(1a) The opinions contained herein are the private ones of the writer and are not to be construed as official or reflecting the views of the Navy Department or the navy service at large.

(2) Willard, *J. Acoust. Soc. Am.*, **19**, 235 (1947).

(3) Pellam and Galt, *J. Chem. Phys.*, **14**, 608 (1946).

(4) Parthasarathy, *Proc. Ind. Acad. Sci. (A)*, **3**, 285, 482, 519 (1936); **4**, 59, 213 (1936).

(5) Bergmann, "Der Ultraschall," 3rd ed., Edwards Brothers, Ann Arbor, Mich., 1944, p. 174.

(6) See, however, (a) Freyer, Hubbard and Andrews, *THIS JOURNAL*, **51**, 759 (1929); (b) Kincaid and Eyring, *J. Chem. Phys.*, **6**, 620 (1938); Kittel, *J. Chem. Phys.*, **14**, 614 (1946).

still avoid earlier errors due to wall effect. At one kilocycle the wave length in many liquids is about one meter, while at one megacycle (the frequency employed in this investigation) the wave length is about one millimeter.

For the present work, thirty liquid alcohols were selected as a suitable group of compounds in which correlations could be made between sound velocity and chemical structure. Specifically, sound velocity is of interest in connection with molecular weight, molecular volume, adiabatic compressibility, and the ratio of specific heats.

Experimental

Each alcohol (of the highest purity commercially available from such sources as Eastman Kodak Co., Connecticut Hard Rubber Company, and Carbide and Carbon Chemicals Corporation) was fractionally distilled through a 40-cm. Widmer column shortly before using; the higher boiling compounds were fractionated at a reduced pressure of about 1 mm. A middle fraction of narrow boiling range was selected in each case.

Sound velocity measurements were made by means of