

### References and Notes

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6. T. S. Price, *Per-Acids and their Salts*, Longmans, Green, London, 1912.
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8. M. M. Richter, "Über das 2.6-Dinitro-hydrochinon," *Ber. Dtsch. Chem. Ges.*, **1916**, *49*, 1398-1401.

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## PRIMARY DOCUMENTS ON NITROHYDROQUINONE

Karl Elbs

"Ueber Nitrohydrochinon," *J. prakt. Chem.* [n.F.], **1893**, *48*, 179-185

Translated by E. J. Behrman, D. M. Behrman, Manuela Davis

Until now, mononitrohydroquinone has only been known in the form of several of its derivatives. Now it is shown that nitrohydroquinone can be made by direct oxidation of *o*-nitrophenol with ammonium peroxydisulfate (1).

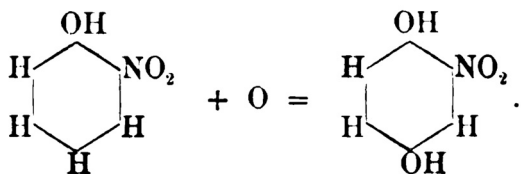
A solution of 35 g [0.25 mol] of *o*-nitrophenol, 50 g [1.25 mol] of sodium hydroxide, and 50 g [0.22 mol] of ammonium peroxydisulfate in 1500 g of water was allowed to stand for 1.5-2 days with occasional shaking. Then the mixture was acidified with sulfuric acid, the unchanged nitrophenol separated by steam distillation, a small amount of resinous material removed by filtration, and then extracted with ether. The ether extract, after evaporation, gave crystals of nitrohydroquinone which after one recrystallization from water or dilute ethanol

is pure. The yield is between 30-40% based on the starting material. Also, about half of the initial nitrophenol was recovered unchanged but increasing the amount of ammonium peroxydisulfate does not increase the yield of nitrohydroquinone but rather diminishes it.

Mononitrohydroquinone crystallizes as rhombohedra or as pyramids which frequently grow together like a cockscomb. The color varies from yellow-red to garnet-red. It melts without decomposition between 133-134° and then solidifies within a few degrees of cooling in crystalline form. There is but slight tendency for sublimation in spite of marked volatility already at 100°. It is not subject to steam distillation. It is very soluble in ether and alcohol, less in acetic acid and hot water, moderately in cold water, hardly at all in benzene, and even less soluble in petroleum ether. It is best crystallized from water or

dilute ethanol. The crystals are water-free; when strongly heated, they explode weakly and leave behind much carbon. Combustion gives 46.8% C & 3.9% H while theory for  $C_6H_3(NO_2)(OH)_2$  is 46.4% C & 3.2% H.

In order to clear up the structure of the oxidation product of *o*-nitrophenol, the molecular weights of the acetate and the benzoate were determined and show that a mononitrodihydroxybenzene is present (2). The attempt to convert the free phenol, the acetate, and the benzoate to the known dinitrohydroquinone or its derivatives was unsuccessful (3). In comparison, methylation yielded without difficulty a monomethyl ether identified as the known nitrohydroquinone monomethylether (4) whereby the position of substitution in the benzene ring for the original oxidation product is established with certainty. The oxidation proceeds according to the equation:

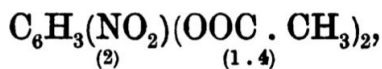


Nitrohydroquinone forms two series of salts which are very soluble except for those with lead, copper, and silver; the solutions of the acid salts are brown while those of the neutral series are violet-blue.

It is difficult to obtain the salts in a pure state for the easily soluble ones are hard to crystallize and they are not very stable in solution. The violet-blue solutions of the neutral salts become dirty brown after a few days and upon acidification give only a little nitrohydroquinone and a brown-black precipitate of variable composition; the acid salts are more stable so that one can easily make the barium salt by heating the nitrohydroquinone with barium carbonate and water.

An oxidation of nitrohydroquinone to the quinone fails just as does that of dinitrohydroquinone. At first, brown, slightly soluble substances with pronounced phenolic character appear, and then decomposition products form.

Diacetylnitrohydroquinone



forms easily by heating nitrohydroquinone with acetic anhydride and fused sodium acetate; the crude product, precipitated from water and thoroughly washed, is best crystallized from aqueous alcohol. There are commonly persistent traces of impurities which lower the melting

point. The diacetate crystallizes in colorless plates or flat prisms or in long, thin, shiny needles by rapid precipitation from 95% ethanol; it is insoluble in water; very soluble in hot ethanol, and moderately soluble in ethanol at room temperature. It melts at 86° and solidifies in a crystalline state upon cooling. A small amount can be distilled almost without decomposition. The molecular weight was determined by freezing point depression in naphthalene and gave 228 whereas 239 is calculated for the formula,  $C_6H_3(NO_2)(OOC \cdot CH_3)_2$ .

The diacetate is slowly saponified with cold dilute sodium hydroxide and it dissolves with a violet-blue color; upon acidification, the color changes to yellow-red and nitrohydroquinone can be recovered upon extraction with ether.

Cold, aqueous ammonia leads to a step-wise saponification; at first a yellow-brown solution which contains the ammonium salt of the monoacetate is formed; later, the second acetyl group is cleaved and the pure violet solution now contains only the neutral ammonium salt of the nitrohydroquinone. The diacetate dissolves easily in cold concentrated sulfuric acid to give a yellow color. By adding water, a red-yellow solution is formed from which pure nitrohydroquinone is obtained by extraction with ether.

The behavior with nitric acid of specific weight 1.5 is peculiar; at 0° the material dissolves easily. If the solution is poured onto ice after standing for a few hours, the unchanged diacetate precipitates as long as the temperature does not rise appreciably above 0°. But if one interrupts the cooling and allows the temperature to rise to 15-20°, a slow release of gas takes place with complete decomposition. Other than a little oxalic acid nothing else was found. The deep yellow color of the liquid is due to a small amount of a phenolic material.

Dibenzoylnitrohydroquinone,  $C_6H_3(NO_2)(OOC \cdot C_6H_5)_2$ , is easily made by shaking the nitrohydroquinone with benzoyl chloride and sodium hydroxide solution. One may only use dilute solutions of sodium hydroxide which are added in small amounts as the formed compound is easily split and must be worked up quickly. The crude material is easily purified by crystallization from boiling ethanol. It is not soluble in water, slightly in hot benzene, moderately in boiling ethanol. The difference in solubility between the boiling point and room temperature is very large for benzene and ethanol. The compound crystallizes in colorless needles which precipitate from benzene as large half spheres; they melt without decomposition but not very sharply between 140-142°

and char at higher temperatures without distilling. The dibenzoate behaves exactly like the diacetate with concentrated sulfuric acid; by contrast, it is somewhat more resistant to alkalis; with hot ammonia it only gives traces of saponification. The freshly prepared material is gradually decomposed by boiling sodium carbonate solutions. Cold dilute sodium hydroxide gradually decomposes the freshly prepared material but not the material dried at 100°. Saponification takes place rapidly in alcoholic sodium hydroxide solutions.

The freezing point depression in naphthalene gave molecular weights of 391, 349, 381, and 343 for an average of 366; the formula weight of  $C_6H_3(NO_2)(OOC.C_6H_5)_2$  is 363.

Dibenzoylnitrohydroquinone is dissolved in nitric acid, sp. g. 1.5, at 0° and allowed to stand for 6 hours while the temperature rises to 26°. The mixture is then poured onto ice. A yellow precipitate forms which is hardly soluble in the usual solvents but which can be crystallized from boiling ether or acetic acid. One obtains a colorless crystalline sandy powder. The substance melts unchanged at 218-220° and remains crystalline upon cooling. It explodes weakly when heated strongly on a platinum plate; it dissolves in cold concentrated sulfuric acid and precipitates unchanged upon the addition of water. Moderately dilute sodium hydroxide solutions give slow saponification and the formation of a violet solution. The addition of sulfuric acid gives a precipitate of not wholly pure m-nitrobenzoic acid while extraction of the yellow-red solution with ether gives nitrohydroquinone. It follows that under these conditions a nitration occurs, but only for the benzoyl groups, not in the desired way of forming an ester of dinitrohydroquinone. The nitration product consists, for the most part, of di(m-nitrobenzoyl) nitrohydroquinone.

A mixture of 6 g nitrohydroquinone, 6 g methyl iodide, 3 g KOH, and 20 g methanol was heated at 100° in a sealed tube for six hours. The contents become dark brown. They are weakly acidified and steam distilled. One obtains 2.1 g of material whose chemical and physical properties agree wholly with those obtained in a different way by Weselsky and Benedikt (4) for nitrohydroquinone monomethyl ether. (The mass consists of large, flat prisms obtained after gradual evaporation of the solution. In the process, due to the weakly acidic character, the ammonia gradually escapes). After the separation by steam distillation, the cooled residue is separated from some resinous material and the filtrate extracted with ether whereby 1.6 g of unchanged nitrohydroquinone was recovered. From the mother liquor of

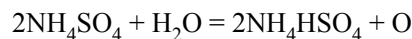
recrystallized monomethylether, a very small amount of yellow needles was identified as the dimethyl ether because of their insolubility in alkali and melting point 71°.

Because of the similarity which mononitrohydroquinone and common dinitrohydroquinone show, it is important to emphasize their differences.

Mononitrohydroquinone crystallizes water-free. Its neutral barium salt is very soluble; its acid methyl ether crystallizes in orange-yellow prisms, melting point 83°, and is very volatile in steam; its diacetate crystallizes in colorless needles, melting point 86°.

Dinitrohydroquinone crystallizes with 1.5 moles of water; its neutral barium salt forms black needles nearly insoluble in water; its acid methyl ether crystallizes in cloudy greenish needles, melting point 102°, which are not volatile in steam; its diacetate crystallizes in sulfur-yellow needles, melting point 96°.

The relatively smooth conversion of nitrophenol to nitrohydroquinone shows that this oxidation by peroxydisulfate is a new method that will prove useful in many cases. It can be used in acid, alkaline, and neutral solution [wrong] and brings oxygen to work in the sense of the equation:



Also, the fact that the oxidation agent is colorless and works without giving a precipitate is a factor of importance. This material is not yet commercially available and so in the following paper I describe a good method for its preparation [pp. 185-188].

## References and Notes

1. For the preparation of ammonium peroxydisulfate see the following communication [not translated here, but see pp. 23-24 of T. S. Price, *Per-Acids and their Salts*, Longmans, Green & Co., London, 1912 which reproduces a translation of Elbs' preparation of ammonium peroxydisulfate taken from R. S. Hutton's translation of Elbs' book *Electrolytic Preparations* (Edward Arnold, London, 1903).]
2. Goldstein (Ber. 7, 734) obtained a dinitrodiphenol  $NO_2.C_6H_3(OH)-(OH)C_6H_3.NO_2$  by oxidation of o-nitrophenol with potassium permanganate. [?]
3. Strecker, Ann. Chem., **118**, 293; Nietzki, Ber. **11**, 470; Ann. Chem. **215**, 143; Hesse, Ann. Chem., **200**, 245. [These papers concern 2,6-dinitrohydroquinone made in connection with the structure of arbutin.]
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