

THE INFLUENCE OF MOLYBDATES ON THE HYDROGEN  
PEROXIDE OXIDATION OF NAPHTHALENE AND  
 $\beta$ -NAPHTHOL<sup>1</sup>

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Molybdates, as well as oxides and salts of other so called "peracid formers" such as tungsten, vanadium, titanium, zirconium, and tantalum, in the presence of hydrogen peroxide are known to be very specific oxidants for certain inorganic reactions of hydrogen peroxide (1). Furthermore, organic acids such as formic and acetic which are capable of forming peracids have behaved in the same manner as the metallic peracids in several instances.

The use of peracetic and perbenzoic acids as oxidizing agents in organic chemistry is well known, but only in a few cases have molybdates been used with hydrogen peroxide in the oxidation of organic compounds. Toennies and Kolb (2) oxidized methionine to methionine sulfone with hydrogen peroxide and a mixture of perchloric acid and ammonium molybdate; Larsson (3) found that the oxidation of thioacetic acid and  $\beta, \beta'$ -thiodipropionic acids to the corresponding sulfoxides and sulfones by hydrogen peroxide proceeded rapidly in the presence of molybdic acid. In both cases, however, the amount of molybdate used seemed excessive and its use as a catalyst in hydrogen peroxide oxidations, by no means recognized. One of the few examples where molybdate was used catalytically is the oxidation of acetaldehyde to acetic acid by hydrogen peroxide in the presence of molybdenum trioxide or vanadium pentoxide, described by Takigawa (4) in an analytical volumetric procedure for the determination of acetaldehyde. Milas and co-workers (5) in their work on the hydroxylation of the unsaturated substances have recognized the possibilities of the peracids as selective catalysts and have extended their studies to a number of these compounds.

Since the metallic peracids are such selective oxidants for inorganic reactions, a preliminary study of the use of molybdate as a catalyst for the hydrogen peroxide oxidation of organic compounds was made in this laboratory.  $\beta$ -Naphthol was selected for comparative purposes as the reductant for the initial experiments, inasmuch as considerable information regarding its behavior during peracetic acid oxidations has been published.

Boeseken and Koenigsfeldt (6) reported that a good yield of *o*-carboxycinnamic acid, together with a small amount of an unknown substance  $C_{20}H_{14}O_4$ , was obtained by the slow oxidation of  $\beta$ -naphthol using peracetic acid in glacial acetic acid. Greenspan (7) improved this procedure by using a concentrated instead

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of a dilute solution of peracetic acid, which resulted in an almost immediate deposition of crystals of *o*-carboxycinnamic acid.

In this laboratory  $\beta$ -naphthol was oxidized with hydrogen peroxide in glacial acetic, (a) with and (b) without molybdate in the reaction mixture. Without molybdate the reaction occurred very slowly, a precipitate forming after several days, but only after an additional amount of hydrogen peroxide had been added. However, in the presence of molybdate, the reaction was completed in a matter of hours.

Both reaction products (with and without molybdate) upon examination were found to be mixtures of at least two acids. These two acids were easily separated, due to insolubility of the second acidic constituent in sodium bicarbonate solution, into *o*-carboxycinnamic acid and an unknown acid melting at 280–281°. This latter acid had the properties of an acid described by Ehrlich (8), which he obtained in small yield in addition to *o*-carboxycinnamic acid during the oxidation of  $\beta$ -naphthol with dilute permanganate, and to which he assigned the empirical formula  $C_{20}H_{12}O_4$ . According to Ehrlich, the acid melts at 280–281°, is difficultly soluble in alcohol and practically insoluble in other solvents; from the saponification number it appears to be dibasic, but yields only a monosalt and a monoethyl ester.

Later Dischendorfer and Danzigar (9) established the structure of this acid and found it to be 4-(2-carboxyphenyl)-5,6-benzocoumarin. This explains the fact that the compound forms only the monoester and monosalt while it appears to be dibasic on titration. The acid isolated in this laboratory was insoluble in bicarbonate solution and gave a saponification value of half the molecular weight.

It is interesting that Boeseken and Koenigsfeldt reported an uncharacterized by-product ( $C_{20}H_{14}O_4$ , m.p. 265–267°) obtained during the peracetic acid oxidation of  $\beta$ -naphthol, which these workers concluded was one of the bisdihydroxy naphthalenes on the basis of its insolubility in bicarbonate solution.

When  $\beta$ -naphthol was suspended in very dilute hydrochloric acid solution containing a trace of ammonium molybdate and an excess 30% hydrogen peroxide was added slowly, an exothermic reaction started immediately, but instead of proceeding to *o*-carboxycinnamic acid, the solution turned dark red and a black resin (I) precipitated. From the red solution a small amount of an orange-red substance (II) separated on standing. In the absence of molybdate, the same reaction proceeded at a very slow rate; after thirty hours the solution was red and a red precipitate separated. This was found to be mostly unreacted  $\beta$ -naphthol, mixed with a small amount of a fine red precipitate.

The failure to obtain *o*-carboxycinnamic acid indicates that molybdate-catalyzed hydrogen peroxide in glacial acetic acid and in dilute hydrochloric acid (in which permolybdic acid is probably the responsible oxidizing agent) react in a completely different manner, under the prevailing conditions. This may be due to differences in the oxidant, but may also be due to differences in the solvents. There are many examples in the literature that demonstrate the decisive influence of the solvent on the course of the reaction when hydrogen peroxide or the peracids are used as reagents.

The black resin (I) was found to consist of a mixture of (II) and another un-

identified yellow solid. A study of the properties of (II) was then undertaken; the orange compound was found to be soluble in all ordinary organic solvents, in sodium hydroxide, sodium carbonate, and concentrated sulfuric and acetic acids. It was insoluble in sodium bicarbonate and dilute acids. The red alkaline solution turned readily dark, and compound (II) was not reprecipitated with dilute acids in the original form. Compound (II) gave a dark green color in concentrated sulfuric acid and a red color in glacial acetic. Recrystallization from dilute acetone gave shiny dark red crystals. Molecular weight determinations gave an average value of 313, which indicates that condensation of two naphthol molecules must have taken place.

Due to the interesting properties of (II), a series of experiments was undertaken in order to improve its yield. When the reaction was conducted in a homogeneous medium, such as aqueous alcohol or acetone, more satisfactory results were obtained. Water seems to be necessary for the reaction, since the solution only becomes colored after addition of water to the reaction mixture. This might possibly be due to the solubility of the molybdate in the solvents used. The isolation of the product from the reaction mixture when alcohol or acetone were used as solvents, presented a special problem, since the precipitate obtained by pouring the solution into water was always too fine to be filtered. This difficulty was avoided by pouring the reaction mixture into a large volume of water and salting out the orange precipitate, which was then obtained in excellent yields.

Since earlier studies of peracetic acid oxidations of the naphthols had extended to naphthalene (10), similar experiments were conducted with molybdate-catalyzed hydrogen peroxide. Naphthalene has been reported to have been slowly oxidized to *o*-carboxycinnamic acid (10) by peracetic acid. When naphthalene was treated in a glacial acetic acid medium with hydrogen peroxide in presence of ammonium molybdate the reaction proceeded slowly but when heated it started immediately and gave a phthalide, the lactone of 3-(2-carboxyphenyl)-3-hydroxypropanoic acid, in 69% yield as against a 43% yield in the absence of ammonium molybdate.

#### EXPERIMENTAL

*Oxidation of  $\beta$ -naphthol with hydrogen peroxide in glacial acetic acid in the presence of sodium molybdate.*  $\beta$ -Naphthol (20 g., 0.139 mole) and 100–150 mg. of sodium molybdate were dissolved in 120 ml. of glacial acetic acid and 100 ml. of 30% hydrogen peroxide was very slowly added to the stirred material over a period of 4–5 hours. The reaction mixture was stirred an additional twenty hours, cooled in an ice- and salt-bath and then diluted with 200 ml. of cold water to complete the precipitation.

The crude acid product was removed, suspended in a cold saturated solution of sodium bicarbonate, and stirred for one-half hour. The insoluble material was removed, suspended in 50 ml. of cold ethanol to remove soluble impurities, and filtered. The precipitate was decolorized with charcoal and recrystallized from hot ethanol. Yield, 1.2 g. of acid, m.p. 282–283°.

*Anal.* Calc'd for  $C_{20}H_{12}O_4$ : C, 75.9; H, 3.83; Sap. equivalent, 158.

Found: C, 76.2; H, 4.06; Sap. equivalent 160.

The bicarbonate solution after acidification gave 14.1 g. of crude *o*-carboxycinnamic acid, m.p. 172–174°. After decolorization with Norit and recrystallization from a water-ethanol mixture, m.p. 188–190°; yield 11.2 g.

*Anal.* Calc'd for  $C_{10}H_8O_4$ : C, 62.5; H, 4.20; Neutral equivalent, 96.

Found: C, 62.4; H, 3.86; Neutral equivalent, 96.

*Oxidation of  $\beta$ -naphthol with hydrogen peroxide and ammonium molybdate in an aqueous alcohol medium.* To a stirred mixture containing 1 g. of  $\beta$ -naphthol, 25 mg. of ammonium molybdate, 5 ml. ethanol, and 2 ml. glacial acetic acid was added dropwise 1.6 ml. of 30% hydrogen peroxide. This mixture was then saturated with water and after 10–15 minutes was placed in a refrigerator for 2–3 hours until the completion of reaction (this time factor is important in order to obtain an uncontaminated product). Alcohol was then added to dissolve the partially precipitated product. This alcoholic solution in turn was poured into 500–700 ml. of stirred water, which upon treatment with salt, yielded 1 g. of an orange product.

The product was dissolved in acetone, the solution filtered, cooled, and water added to induce crystallization. After standing for two hours at room temperature shiny dark red crystals melting at 148° were obtained.

*Anal.* Calc'd for  $C_{20}H_{14}O_4$ : C, 75.5; H, 4.43; Mol. wt., 318.

Found: C, 75.1; H, 4.40; Mol. wt., 313.

*Oxidation of naphthalene with hydrogen peroxide in the presence of ammonium molybdate.* Naphthalene (10 grams, 0.0782 mole) 0.2 g. of ammonium molybdate, and 250 ml. of glacial acetic acid were placed in a 500-ml., 3-necked flask equipped with a stirrer, reflux condenser, and dropping-funnel. The solution was brought to a gentle reflux and 84.0 g. of 30% hydrogen peroxide was slowly added over a period of four hours. The acetic acid solution was diluted with an equal volume of water, cooled in an ice-bath, and filtered to remove the unreacted naphthalene (2.3 g.). The filtrate was distilled under reduced pressure to remove the solvent and the residue was maintained at 100° for two additional hours to remove the last traces of water and acetic acid.

After several extractions with hot benzene the cooled extractant yielded 8.0 g. of slightly colored solid, m.p. 149–150°; 69% yield (without molybdate, yield 43%). Recrystallization from a *n*-heptane–*n*-amyl alcohol (9:1) mixture gave crystals, m.p. 152°, neutral equivalent 192.5. A mixed melting point of this compound with the sublimate of *o*-carboxycinnamic acid gave no depression.

Greenspan gives m.p. 153° for the lactone of  $\beta$ -hydroxy- $\beta$ -*o*-carboxyphenylpropanoic acid, neutral equivalent 192.0.

#### SUMMARY

The catalytic influence of molybdate salts (2) on hydrogen peroxide oxidations of naphthalene and  $\beta$ -naphthol was demonstrated. The effect of the solvent on the molybdate-catalyzed hydrogen peroxide oxidation of  $\beta$ -naphthol was also illustrated. A new method for the preparation of 4-(2-carboxyphenyl)-5,6-benzocoumarin and a new oxidation product of  $\beta$ -naphthol,  $C_{20}H_{14}O_4$ , are reported.

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