Oxidation of Phenolphthalein with Alkaline Hydrogen Peroxide

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Some time ago it was pointed out¹ that the so-called phenolphthalein oxime cannot possess the structure hitherto assigned to it (I), but is a derivative of 2,3,1-benzoxazine (II).

It can be rearranged and hydrolyzed to *p*-aminophenol and 2-*p*-hydroxybenzoyl benzoic acid.

When in the preparation of the "oxime" an excess of hydroxylamine is present a side reaction occurs with formation of *p*-aminophenol and *N*-*p*-hydroxyphenyl phthalimide¹. The final products after hydrolysis are thus 2 moles of *p*-aminophenol and one of phthalic acid.

Due to the structural similarity between hydroxylamine and hydrogen peroxide it was thought worth while to examine the behaviour of the latter towards phenolphthalein in alkaline solution. It is known² that triphenylmethyl hydroperoxide can rearrange to benzophenone and phenol, so it was thought possible that a similar rearrangement might take place in a reaction with phenolphthalein:

(It could hardly be expected to be possible to isolate a cyclic compound corresponding to phenolphthalein oxime.)

Preliminary experiments showed that the red colour of the alkaline solution of phenolphthalein faded rapidly after addition of hydrogen peroxide. Addition of sodium hydroxide to a suspension of phenolphthalein in 10 % hydrogen peroxide caused a rise in temperature, at first fairly slow, but suddenly extremely rapid, and most of the reaction mixture was thrown out of the flask. In order to get a controlled reaction it was necessary to keep the temperature rather low.

Only the red form of the phenolphthalein anion seems to react with hydrogen peroxide at room temperature. A solution in a large excess of 10 % sodium hydroxide brought to the fading equilibrium was left overnight at 10° after addition of an excess of hydrogen peroxide. On acidification the phenolphthalein could be recovered almost quantitatively.

When carried out under suitable conditions the reaction gave a good yield of hydroquinone; the other product was not, however, the expected hydroxybenzoyl benzoic acid, but phthalic acid, and the yield of hydroquinone could be raised to about 120 % of that calculated for the expected reaction. Obviously the reaction proceeds in a similar way as the side reaction observed with an excess of hydroxylamine:

It is noteworthy that neither hydrogen peroxide nor hydroxylamine reacts with *p*-hydroxybenzoyl benzoic acid in alkaline solution. Obviously the attack of the second molecule of hydrogen peroxide or hydroxylamine sets in at some intermediate stage, the first one having a high and the latter a lower rate of reaction as compared with the rearrangement reaction proper.

The very violent reaction observed in the preliminary experiments seems to be an oxidation of hydroquinone: addition of hydrogen peroxide to an alkaline solution of hydroquinone results in a quite similar phenomenon. How far the oxidation goes has not been ascertained, but at least some carbonic acid is formed.

Other phthaleins react similarly, although with very different velocities. Fluorescein, thymolphthalein, and α -naphtholphthalein react very slowly and the corresponding polyvalent phenols could not be isolated, but were oxidized further. At higher temperatures thymolphthalein gave, besides phthalic acid, fatty acids with the rancid odour of butyric acids.

Experimental: 1. *Phenolphthalein*. In a 3-necked flask provided with a stirrer, a thermometer, and a dropping funnel, phenolphthalein (20 g) is suspended in water (40 ml) and 30 % hydrogen peroxide (10 ml). The flask is placed in a cooling bath. Stirring is started and a 30 % sodium hydroxide solution is added dropwise at such a rate that the temperature is kept at $15 \pm 2^\circ$. After about 15 ml have been added, three 5 ml portions of hydrogen peroxide are added during the addition of some 15 ml of sodium hydroxide more. It may be necessary to add one more portion of hydrogen peroxide when all solid phenolphthalein has

been dissolved. After some standing the red colour of the solution turns brown (due to some oxidation of hydroquinone). The solution is acidified with conc. hydrochloric acid and cooled. A mixture of phthalic acid and hydroquinone separates and is filtered off. The filtrate is extracted twice with ether (100 ml). The ether extract combined with the mass of crystalline material is treated with aqueous potassium hydrogen carbonate. From this extract phthalic acid (9.5 g) separates on acidification. From the ether solution hydroquinone is isolated, yield 8.2 g (59 %).

2. *Fluorescein*. Fluorescein (5 g) is dissolved in 10 % sodium hydroxide (30 ml) and 30 % hydrogen peroxide (10 ml) is added. The flask is cooled under the tap and the temperature is kept at $30\text{--}35^\circ$. More portions (5 ml) of hydrogen peroxide are added when no spontaneous rise of temperature is noticed, until the orange colour of the solution changes to pure yellow. If necessary, sodium hydroxide is added to keep the solution alkaline. Addition of hydrochloric acid causes strong effervescence, indicating the oxidation of the trivalent phenol to carbon dioxide. Phthalic acid (2.1 g), yellow, but otherwise pure can be isolated.

3. *Hydroquinone and hydrogen peroxide*. Hydroquinone (1 g) is dissolved in 10 % sodium hydroxide (15 ml) and 30 % hydrogen peroxide (5 ml) is added. The temperature rises and in less than a minute the liquid boils vigorously.

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2. Wieland, H. and Maier, J. *Ber.* **64** (1931) 1205.

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