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# The Photochemical Addition of Hydrogen Peroxide to the Double Bond

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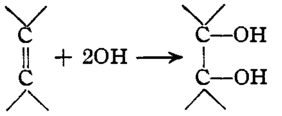
Considerable spectroscopic evidence[3] has recently accumulated to show that light in the region of about 3000 Å. causes the dissociation of hydrogen peroxide into two hydroxyl radicals. However, very little direct chemical evidence exists in favor of the formation of these radicals. Our interest in the hydroxylation of unsaturated substances[4] led us to devise experiments whereby free hydroxyl radicals, produced either by the photochemical dissociation of hydrogen peroxide or by the dissociation of water or hydrogen peroxide in the field of an electrodeless discharge,[5] could be made to react with unsaturated substances to form hydroxylated products in which the hydroxyl groups retain their identity. Essentially, the reactions may be illustrated as follows

$$HOOH + h\nu \longrightarrow 2OH \qquad (1)$$



(2)

Since the life of these radicals is of short duration, the unsaturated substances were either mixed directly with their precursor, hydrogen peroxide, and the mixture exposed to ultraviolet radiation, as in the case of the present experiments, or allowed to meet the hydroxyl radicals in the immediate vicinity of, but not within, the field of the electrodeless discharge. Using the first method, we succeeded in producing glycerol from allyl alcohol, dihydroxybutyric acid from crotonic acid, mesotartaric acid from maleic acid, and diethyl mesotartrate from diethyl maleate. It was not possible to produce these dihydroxy substances when the mixtures were allowed to stand in the dark, and their production therefore is attributed to the presence of hydroxyl radicals in the photochemical reaction. That free hydroxyl radicals react in this fashion was also shown by the second method in which ethylene glycol was produced from ethylene.[5]

## Experimental Part

A Cooper–Hewitt mercury vapor lamp was used in all of our experiments at a distance of 50 cm. from the quartz vessel containing the reaction mixtures. The latter was surrounded with an aluminum reflector in such a way that maximum utilization of the necessary light was effected. To ensure a greater surface, shaking of the reaction vessel during radiation was found beneficial in some experiments. An electric fan was allowed to play on the reaction vessel, thereby preventing a rise of temperature above that of the room.

The hydrogen peroxide used in many of the experiments was prepared either by the method of Rice, Reiff and Kilpatrick,[6] or that of Hurd and Puterbaugh,[7] and appropriate dilutions were made from this. Parallel experiments of the same concentration of the reactants were conducted in the presence and absence of ultraviolet light and the rate of the disappearance of hydrogen peroxide was determined in each case. Preliminary experiments were first made in 70 and 30% solutions of hydrogen peroxide, respectively, with maleic and crotonic acids, but the oxidation was much too destructive to permit isolation of the hydroxy compounds. Best results were finally obtained in a solution of about 10% hydrogen peroxide. In the dark, the reactions were not only slow, but in no case were we able to isolate the dihydroxy compounds. The 70% solution of hydrogen peroxide oxidized maleic acid rapidly in the dark, but attempts to isolate mesotartaric acid were not successful.

**Glycerol from Allyl Alcohol.**—Ten grams of allyl alcohol was mixed in a quartz flask with a solution of 10% hydrogen peroxide in the molal ratio of 1:1.05, and the mixture exposed to ultraviolet light under shaking at about 100 strokes per minute. At the end of one hundred and sixty-eight hours, the mixture had lost 89% of its peroxide content while the sample in the dark remained the same. To separate the glycerol formed, the mixture was subjected to fractional distillation and the fraction (6.8 g.) boiling at 287–289° collected. This corresponds to a yield of 43% based on the amount of alcohol used. Since there was no carbon dioxide evolved during the reaction and most of the unreacted allyl alcohol recovered, the yield of glycerol was actually considerably higher. It may also be seen that for every mole of hydrogen peroxide reacted there was approximately one mole of peroxide decomposed to oxygen and water.

**Dihydroxybutyric Acid from Crotonic Acid.**—Ten grams of crotonic acid (Eastman Kodak Company) was mixed in a quartz flask with 70 cc. of 5.8% solution of hydrogen peroxide and the mixture exposed to ultraviolet light while

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(1) B.S. Thesis, M. I. T., 1935.

(2) B.S. Thesis, M. I. T., 1936.

(3) Urey, Dawsey and Rice, THIS JOURNAL, **51**, 1371 (1929); von Elbe, *ibid.*, **55**, 62 (1933); Rodebush and Wahl, *J. Chem. Phys.*, **1**, 696 (1933); Oldenberg, *ibid.*, **3**, 266 (1935); Frost and Oldenberg, *ibid.*, **4**, 642, 781 (1936); Kondratjew and Zinskin, *Acta Physicochim. U. R. S. S.*, **5**, 301 (1936).

(4) Milas and Sussman, THIS JOURNAL, **58**, 1302 (1936).

(5) Milas, Stahl and Dayton, unpublished results.

(6) Rice, Reiff and Kilpatrick, THIS JOURNAL, **48**, 3019 (1926).

(7) Hurd and Puterbaugh, *ibid.*, **52**, 950 (1930).

shaking at about 100 strokes per minute. At the end of one hundred and seventy hours, the mixture had lost 77% of its peroxide content while the mixture in the dark remained the same. The products were separated following the method of Braun.[8] The unreacted crotonic acid was separated by extraction with chloroform and the residual solution concentrated at room temperature under reduced pressure. The viscous sirup thus obtained was further dried for twenty-four hours in a vacuum oven at 40° and at a pressure of 2 mm. The highly viscous sirup (4.2 g.) thus obtained corresponded to a 30% yield of dihydroxybutyric acid based on the total amount of crotonic acid used. Two samples of this were then titrated against a standard alkali and gave an average neutralization equivalent of 119 which is in close agreement with the calculated value of 120 for dihydroxybutyric acid.

A small amount of destructive oxidation also took place since both carbon dioxide and acetaldehyde were detected in the reaction mixture.

**Mesotartaric Acid from Maleic Acid.**—Several experiments were carried out with maleic acid using concentrated hydrogen peroxide solutions, but in all cases the oxidation was too destructive, yielding copious quantities of carbon dioxide and products not easily identifiable. Finally, 10 g. of maleic acid was dissolved in 53 cc. of 5.8% hydrogen peroxide solution and the latter exposed to ultraviolet light under similar conditions as in the previous cases. After one hundred and twenty-two hours, the solution had lost about 88% of its original strength of hydrogen peroxide while the dark reaction lost only 12% of its strength. When the products of the photochemical reaction were worked up following the method of Milas and Sussman,[4] a yield of 4.65% of mesotartaric acid was obtained. In another experiment in which the reaction was allowed to proceed only for thirty hours, the yield of mesotartaric acid was 9% of the total maleic acid used. The calcium salt of the mesotartaric acid obtained was purified by reprecipitation and dried in an oven for twenty-four hours at 105°.

*Anal.* Calcd. for $C_4H_4O_6Ca$: Ca, 21.28. Found: Ca, 21.05, 21.09, 21.52.

The dark reaction yielded no mesotartaric acid. This observation is in accordance with the findings of Hatcher and Mueller.[9]

**Mesotartaric Acid from Diethyl Maleate.**—The diethyl maleate was prepared by refluxing for four hours a mixture of 100 g. of maleic acid, 250 cc. of absolute ethyl alcohol and 20 g. of sulfuric acid (sp. gr. 1.84), then cooling and pouring the mixture into cold water. The ester was separated, washed with five successive 40-cc. portions of saturated sodium bicarbonate solution and fractionated; the fraction boiling from 219 to 220° (uncorr.) was collected and used in our experiments. The b. p. of this ester is given in the literature[10] as 225° (corr.). Inasmuch as this ester is insoluble in water, anhydrous solutions of hydrogen peroxide in ether or tertiary butyl alcohol were mixed with it in such proportions that the molal ratio of the ester to hydrogen peroxide was 1:1.05. The solvents were then removed under reduced pressure and the residual mixture irradiated as before. At the end of one hundred and twenty-two hours, the reaction mixture was hydrolyzed by refluxing with a solution of 10% alcoholic potash. The alcohol was then removed by distillation, the residue neutralized with dilute hydrochloric acid and the resulting solution made ammoniacal. From this, the mesotartaric acid was precipitated as calcium mesotartrate. A yield of 21.7% calculated as diethyl mesotartrate was obtained. The amount of destructive oxidation, as judged by the amount of carbon dioxide produced, was considerably less than in the case of maleic acid.

## Summary

1. It has been shown that hydrogen peroxide, under the influence of ultraviolet light, reacts with double bonded compounds to form the corresponding glycols.

2. Glycerol, dihydroxybutyric acid, mesotartaric acid and diethyl mesotartrate have been obtained from allyl alcohol, crotonic acid, maleic acid and diethyl maleate, respectively.

3. The formation of glycols, in the present case, is assumed to take place through the addition to the double bond of free hydroxyl radicals which are formed by the dissociation of hydrogen peroxide under the influence of ultraviolet light.

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[8] Braun, THIS JOURNAL, **51**, 228 (1929).

[9] Hatcher and Mueller, *Can. J. Research*, **3**, 291 (1930).

[10] Anschütz, *Ber.*, **12**, 2283 (1879).