

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MCGILL UNIVERSITY]

## APPLICABILITY OF THE QUINHYDRONE ELECTRODE TO UNSATURATED ACIDS

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In the course of studies of the reaction of hydrogen peroxide on organic substances, it was found necessary to prepare dihydroxymaleic acid, and the method used was that of Fenton,<sup>1</sup> more recently detailed by Nef.<sup>2</sup> The technique of this method after many trials was found to be so unsatisfactory, and experiments performed on the purified product showed such conclusive evidence of further reaction with hydrogen peroxide, that it was decided to study the mechanism of the Fenton Reaction in this particular.

Briefly stated, this reaction results from treating tartaric acid with dilute hydrogen peroxide in the presence of ferrous sulfate, the dihydroxymaleic acid being precipitated by fuming sulfuric acid later. It was found possible to increase the very small yields characteristic of this reaction; but, after many experiments involving every possible variation of conditions governing the reaction, definite data were obtained to show that it was the hydrogen-ion concentration of the mixture which prevented more than one-third of the theoretical quantity of hydrogen peroxide from reacting to form dihydroxymaleic acid. It was planned to decompose the excess peroxide by means of platinum black and to employ the very convenient quinhydrone electrode to determine the hydrogen concentration of the mixtures of dihydroxymaleic and tartaric acids produced during the course of the reaction. That this method was unsuitable is shown in the following data. It should be added, however, that further experiments now nearing completion justify the previous ideas as to the very important part played in this reaction by hydrogen ions.

Biilmann and Lund<sup>3</sup> were responsible for the development of the quinhydrone electrode method for  $P_H$  determination in acid solution, and they recommended its use because of the simplicity of its technique and because of its superior applicability over the hydrogen electrode to unsaturated compounds. It is shown below that the quinhydrone electrode is not applicable when the tendency of the solution to reduce is such that the ratio of hydroquinone to quinone is seriously altered.

Very often, however, advantage may be taken of the slowness with which some such oxidation-reduction potentials attain equilibrium. Such acids as maleic and fumaric fall into the class of substances whose  $P_H$  may be thus determined. When the equilibrium is instantaneously or rapidly

<sup>1</sup> Fenton, *J. Chem. Soc.*, 75, 575 (1899).

<sup>2</sup> Nef, *Ann.*, 257, 290 (1907).

<sup>3</sup> Biilmann and Lund, *Ann. chim.*, [9] 15, 109 (1921); [9] 16, 321 (1921).

attained, the method is useless. Such unusual ease of reduction has been found in the case of dihydroxymaleic acid.

### Experimental

Preliminary experiments using dihydroxymaleic acid and the usual amount of quinhydrone (approx. 0.01–0.02 g.) showed that no constant value could be immediately obtained. The readings were at first low, increasing to a maximum and then falling off to a constant level. Addition of further quinhydrone caused a repetition but a slightly higher final level was attained, and so on until addition of still more quinhydrone caused no further change.

TABLE I  
DIHYDROXYMALEIC ACID, 0.00825 *M*

Quinhydrone added in five portions of 0.02 g. each (0.02 g. of quinhydrone was found sufficient to take a second solution of 0.06585 *M* maleic acid to a constant reading of 319.5 millivolts in 30–45 sec.)

Time	No. 1	No. 2	No. 3	No. 4	No. 5
15 Sec.	163	180	233	260	266
30 Sec.	145	168	243	264	267
45 Sec.	...	152	245	264	270
60 Sec.	132	152	251	264	270
1.5 Min.	132	152	251	265	270
2.5 Min.	<sup>a</sup>	<sup>b</sup>	<sup>c</sup>		
15 Min.	132	152	251	265	270.5

<sup>a</sup> Quinhydrone gone in 45 sec. Soln. then colorless. <sup>b</sup> Soln. colorless in 60 sec.  
<sup>c</sup> Faint yellow color remaining at end of 2 min.

**Confirmation of Assumption that the Dihydroxymaleic Acid is Reduced to Tartaric Acid by the Hydroquinone.**—0.0376 g. of dihydroxymaleic acid on reduction would give  $0.0376 \times (150/184) = 0.03065$  g. of tartaric acid.

TABLE II  
TARTARIC ACID. CONC. 0.03065 G. IN 24.84 Cc.

Time, sec.	No. 1	No. 2	Time, min.	No. 1	No. 2
15	260	263	1.5	270	271
30	265	267	2.5	270.5	271
45	268	270	5	270.5	271
60	268.5	271	15	270.5	271

### Discussion of Results

The results with dihydroxymaleic acid show that the quinhydrone electrode cannot be used in the case of this unsaturated acid; 0.02 g. of quinhydrone is sufficient to produce a uniform and constant pressure of hydrogen under ordinary conditions. No constant readings could be obtained using this acid until more than three or four times the above amount of quinhydrone had been added. The obvious conclusion is that there has been reaction between the quinhydrone and dihydroxymaleic acid. Since

hydroquinone is a reducing agent and dihydroxymaleic acid possesses a double bond, it is quite reasonable to suppose that the acid is reduced to tartaric. That such is the case is shown in the last table, in which tartaric acid was used in such a concentration as would result when 0.0376 g. of dihydroxymaleic acid is reduced at the ethylene linkage.

Moreover, assuming that each gram molecule of quinhydrone contributes 2 g. of hydrogen, 0.08 g. would provide 0.00073347 g. of hydrogen; 0.0376 g. of dihydroxymaleic acid requires 0.0004087 g. of hydrogen and constant readings should be obtained using this amount; 0.06 g. would supply 0.0004396 g. of hydrogen for the reduction of the acid and the remaining 0.02 g. produces the pressure of hydrogen ions at the electrode.

Pirie and Pinhey<sup>4</sup> have observed that glutathione, a substance well known to be very easily oxidized and reduced, has a similar effect in upsetting the quinone-hydroquinone equilibrium. Dihydroxymaleic acid, therefore, may be compared to glutathione with respect to the ease with which it may be reduced.

### Conclusion

It is shown above that the quinhydrone electrode is not applicable to all unsaturated acids.

From the standpoint of a study of this acid, the results are doubly interesting since they indicate the reactivity of this double bond, heavily laden as it is with highly negative groups.

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## PREPARATION OF SOME CYCLOPENTANE DERIVATIVES

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Alicyclic compounds are known to be present in many crude petroleum products as well as in a variety of other natural substances. When their diversity and the number of their theoretically possible modifications are considered, our knowledge of them seems relatively meager. In the present work a study has been made of the reactions between cyclopentylmagnesium halides and a variety of aldehydes. Previous employment of the former in the Grignard reaction has been confined to a very few instances, cyclopentylsulfonic acid,<sup>2</sup> cyclopentylcarboxylic acid,<sup>3</sup> cyclopentyl carbinol<sup>3,4</sup> and  $\gamma$ -cyclopentylpropanol<sup>5</sup> having been made thereby.

<sup>4</sup> Pirie and Pinhey, *J. Biol. Chem.*, **74**, 323 (1929).

<sup>1</sup> From the Ph.D. dissertation of W. R. Edwards, Jr., 1928.

<sup>2</sup> Borsche and Lange, *Ber.*, **40**, 2220 (1907).

<sup>3</sup> Zelinsky, *ibid.*, **41**, 2627 (1908).

<sup>4</sup> Wood and Scarf, *J. Soc. Chem. Ind.*, **42**, 13T (1923).

<sup>5</sup> Adams and Noller, *THIS JOURNAL*, **48**, 1080 (1926).