THE EQUILIBRIUM BETWEEN MUCIC ACID AND ITS LACTONES¹

BY W. A. TAYLOR AND S. F. ACREE

In taking up the study of the mechanism of the reactions involved in the oxidation and reduction of sugars and their derivatives, it became necessary to study the equilibrium between the sugar acids and their dehydration products, including the lactones.

In attempting to determine the solubility of mucic acid in water we found that some lactone was formed in the solution at once and that the amount of lactone was greatly increased if the solution were boiled. We also saw that after some time equilibrium was established between the acid and lactone.

A quantitative study of this equilibrium was then taken up. In this work we made up three different solutions of mucic acid at different temperatures. In all three instances we had an excess of acid present. The first was made up at room temperature, the second was kept at 30° for one hour, and the third at 100° for 30 minutes. All three were placed in a constant temperature bath at 25° and shaken from time to time. Measured quantities were withdrawn from each for titration after definite time periods. A piece of filter paper was tied over the end of the pipette to keep the solid particles of acid from being drawn up. It was found that if the solution were poured into ice water the mucic acid could be titrated with standard alkali without affecting the lactone. To determine the amount of lactone present in the solution an excess of standard alkali was added, the solution boiled for a few minutes, and the excess alkali titrated with *N*/10 hydrochloric acid. Phenolphthalein was used as the indicator.

In the following table we give the time *t* in hours, the

¹ Contribution from the Chemical Laboratory of Johns Hopkins University.

amount of $N/10$ alkali necessary to neutralize the free acid and the amount necessary to neutralize the lactone. The amount of the solutions withdrawn for titration was, in each case, 25 cc.

Solution Made Up at Room Temperature

t	Cc alkali necessary to neutralize acid	Cc alkali necessary to neutralize lactone
2	1.63	0.25
4.5	1.70	0.68
28.5	1.65	0.81
52	1.60	1.00
100	1.62	1.16
172	1.64	1.46
258	1.55	1.85
720	1.55	2.13
1440	1.65	3.39

Solution Kept at 30° for 1 Hour

t	Cc alkali necessary to neutralize acid	Cc alkali necessary to neutralize lactone
3	1.90	0.80
26	1.82	0.78
50	1.70	0.90
74	1.68	1.20
146	1.67	1.42
242	1.65	1.69
1440	1.65	3.21

Solution Kept at 100° for 30 Minutes

t	Cc alkali necessary to neutralize acid	Cc alkali necessary to neutralize lactone
3	20.93	19.07
5	19.63	18.95
27	11.12	19.50
51	8.46	17.02
99	7.12	17.62
171	6.00	16.75
267	5.40	14.55
1440	3.76	9.99
2880	1.66	3.42

From these data it is seen that practically the same equilibrium is reached in all three experiments, the first two solutions taking 1,440 hours, while for the third it required 2,880 hours, because of supersaturation phenomena. At equilibrium it required 1.65 cc of alkali to neutralize the free acid and an average of 3.34 cc to neutralize the lactone, so that there are almost exactly twice as many lactone groups as of the carboxyl groups in the solution. It will also be seen from the table that the amount of acid in the first two solutions remains nearly constant throughout, while the amount of lactone steadily increases. In the third solution both the acid and lactone gradually decrease in amount. Whether this lactone is the mono- or di-lactone, or both, we cannot tell from the data but we shall investigate the reaction velocities of the mucic acid, its mono-lactone, and its di-lactone, and shall study some of the monobasic acids to follow the rate of formation of the lactone in those cases in which we can have only the mono compound resulting.

Mr. B. A. Beatty is continuing this investigation under our joint direction, by the use of both conductivity methods and those outlined above, in order to learn whether acids catalyze these changes through the action of the hydrogen ions, or the nonionized molecules, or both.

*Department of Chemistry of Forest Products
University of Wisconsin
Madison*