[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Mechanism of Lactone Hydrolysis

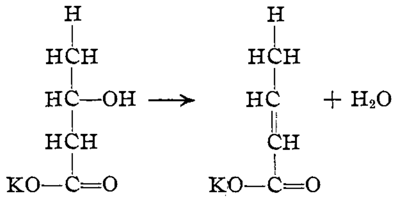
BY A. R. OLSON AND J. L. HYDE

According to Olson and Miller,[1] the hydrolysis of a lactone may proceed by a number of different paths, the actual path followed depending in a great measure on the *p*H of the hydrolyzing solution. Using optically active β-butyrolactone, they showed that the hydroxybutyric acid produced in water had the opposite sign of rotation from that produced in alkaline or in strong acid solution.

The mechanism of hydrolysis which they postulated rests upon the concept of a simultaneous association and dissociation with an inversion for every substitution.[2] This denies the intermediate formation of a carbonium ion in this reaction. Since we do not think of molecules or ions as having fixed boundaries, the theory states that the central carbon atom always is so strongly under the influence of the departing group, the entering group, or both, that the central residue cannot exhibit the properties of an independent existence. Rørdam[3] in a series of papers presented his studies on the hydrolysis of optically active malolactonic acid by which optically active malic acid was produced. He interpreted his results by assuming that the lactone ring was ruptured to produce a carbonium ion, which oscillated from one tetrahedral configuration to its mirror image. The addition of water was thought of as a follow reaction. If the addition occurred in one phase of the oscillation, one optical form of malic acid was produced, if in the other phase, the opposite form was produced. The relative probability of addition in the two phases depended upon the *p*H of the hydrolyzing solution.

These divergent viewpoints apply to many reactions at the present time, and so we wish to point out that the use of heavy oxygen water for hydrolysis furnishes another method of attack on this problem. Thus if the act of hydrolysis of a lactone containing normal oxygen involves a breaking of the bond between the lactone oxygen and the carboxyl carbon, the entering (isotopic) oxygen should be found on the carboxyl carbon, the oxygen on the β-carbon being normal, whereas if the bond between the β-carbon and the lactone oxygen breaks, the isotopic oxygen should be found on the β-carbon. The position of the isotopic oxygen in the hydroxybutyric acid should thus depend upon the *p*H of the hydrolyzing solution if Olson and Miller's[1] mechanism is correct, whereas the carbonium ion theory of Rørdam would require that the isotopic oxygen always be found on the β-carbon atom.

Fortunately the salt of β-hydroxybutyric acid decomposes at moderate temperatures to form water and presumably a crotonate, *e. g.*



$$\begin{array}{c} \mathrm{H} \\ | \\ \mathrm{HCH} \\ | \\ \mathrm{HC{-}OH} \\ | \\ \mathrm{HCH} \\ | \\ \mathrm{KO{-}C{=}O} \end{array} \longrightarrow \begin{array}{c} \mathrm{H} \\ | \\ \mathrm{HCH} \\ | \\ \mathrm{HC} \\ \| \\ \mathrm{CH} \\ | \\ \mathrm{KO{-}C{=}O} \end{array} + H_2O$$

The water which is evolved can then be examined for O^{18} content by published procedure. If this analysis is to be significant, the oxygen in the water must not be permitted to exchange with the oxygen of the carboxyl groups. Excess alkali during the decomposition slows down the rate of this exchange. However, excess alkali has another effect. It acts upon the crotonate in the presence of the moisture to produce hydrogen gas and presumably carbonate and acetate. We therefore had to determine the best experimental compromise between these two effects.

Experimental

The lactone was prepared in this Laboratory by Mr. T. R. Simonson using the method described by Johansson.[4] The isotopic water was obtained from Professor Merle Randall. It was distilled from alkaline permanganate before use. The O^{18} content of the water was determined by the method of Cohn and Urey.[5] The analyses by the mass spectrometer, which was constructed in this Laboratory, were accurate to about one per cent. In making a run, 0.40 cc. of the lactone was dissolved in 10.0 cc. of heavy oxygen water of known isotopic content. This solution was kept at 25° until at least 99% had hydrolyzed as calculated from Olson and Miller's rate constants. The change in *p*H was determined in a separate experiment by indicators. After hydrolysis a small amount of phenolphthalein was added and the solution neutralized by addi-

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[1] Olson and Miller, THIS JOURNAL, **60**, 2687 (1938).

[2] Olson, *J. Chem. Phys.*, **1**, 418 (1933).

[3] Rørdam, *J. Chem. Soc.*, 2447 (1928); 1282 (1929); 2017 (1930); 2931 (1932).

[4] Johansson, *Ber.*, **48**, 1256 (1915).

[5] Cohn and Urey, THIS JOURNAL, **60**, 679 (1938).

tion of potassium hydroxide and hydrochloric acid. Any desired excess of potassium hydroxide was then added and the water distilled off *in vacuo*. The solid residue was pumped for three hours under high vacuum while kept at 100° by a water-bath.

The water-bath was then replaced by an oil-bath maintained at 200 ± 3° for several hours to decompose the salt. The water formed by the decomposition was distilled *in vacuo* as rapidly as possible into a tube of known volume which was cooled by a carbon dioxide–acetone bath. A known amount of carbon dioxide was then admitted to the tube containing the solid water, after which the tube was sealed off. It was then shaken for thirty-six hours at room temperature, in order to get complete isotopic exchange between the carbon dioxide and water, and finally the carbon dioxide was analyzed in the mass spectrometer. The weight of water was determined from the weights of the filled and the empty tube and the weight of the carbon dioxide. This permits a calculation of the O^{18} content of the water before exchange with the carbon dioxide. The differences between the values found and the normal isotopic content of water were expressed as percentages of the maximum possible difference, *i. e.*, the difference between the isotopic content of the hydrolyzing water and normal water. These values are listed in the tables as the "per cent. apparent water mechanism." In those experiments where hydrogen was produced during decomposition of the hydroxybutyrate, it was pumped off before admitting the carbon dioxide.

The solid residue left after the thermal decomposition was dissolved in water, and divided into two equal parts. One part was titrated potentiometrically with 0.1 *N* hydrochloric acid after adding a known amount of sodium hydroxide in order to detect any change in the amount of acid groups. The amount of unsaturation was determined by acidifying the other half with hydrochloric acid, adding a standard bromate–bromide solution, and determining the excess bromine after five minutes.

The series of experiments summarized in Table I, where the hydrolyses had been conducted in heavy oxygen water without acid or alkali added, demonstrated the dependence of the "apparent water mechanism" on the amount of excess alkali present during decomposition, *i. e.*, the exchange reactions between water and carboxyl group mentioned above. In all later experiments we used 4 mole per cent. excess alkali (0.20 millimole).

We then varied the conditions under which the lactone was hydrolyzed, keeping the conditions for the subsequent decomposition constant. These experiments are listed in Table II where we include Experiment 33 from Table I for comparison. Other experiments in buffer solutions were tried, but the results were erratic. Part of the trouble may be due to exchange reactions, and part of it to specific reactions of the ions with the lactone such as those mentioned below.

Discussion of Results

Olson and Miller pointed out that carbonate ion and phosphate ions must have specific effects not

Table I

Change in Percentage Apparent Water Mechanism with Excess Alkali Content during Thermal Decomposition of Potassium β-Hydroxybutyrate

Hydrolysis in pure (heavy oxygen water) water of 4.9 millimoles β-butyrolactone in 10 cc. of water; *p*H 5 → 2.2

	Milli-equivalents excess alkali					Atomic per cent. O^{18}		
Expt.	Before decomp.	After decomp.	Milliequiv. carboxyl after decomp.	Millimoles double bonds after decomp.	Millimoles water recovered	Orig. water	Recov. water (calcd. prior to exchange with CO_2)	Per cent. apparent water mechanism
30	0	−0.026	4.8	2.6	3.94	0.79	0.565	62
34	0.05	− .016	4.7	2.6	3.48	.84	.68	75
32	.10	− .018	4.8	2.6	3.87	.84	.75	86
33	.20	+ .018	4.8	3.9	4.27	.84	.775	90
35	.30	.062	4.5	3.6	3.82	.84	.77	89
36[a]	.50	.104	5.2	4.0	3.58	.84	.77	89
39[b]	1.00	.188	5.4	3.3	1.81	.83	.805	96
21[b]	5.10	3.41	6.8	...	0.16	Insufficient recovery for analysis		

[a] Hydrogen gas evolved in small amount during decomposition. [b] Hydrogen gas evolved in considerable amount during decomposition.

Table II

Hydrolysis of β-Butyrolactone in Solutions of Various Hydrogen Ion Concentrations

4.9 millimoles β-butyrolactone + 10 cc. of water containing acid, alkali, etc.; 0.20 millimoles excess KOH added after neutralization (before decomposition)

						Atomic per cent. O^{18}			Per cent. apparent water mechanism	
Expt.	*p*H	Solution	Milli-equiv. carboxyl after decomp.	Milli-moles double bonds after decomp.	Milli-moles water recov.	Original water	Solution (calcd.)	Recov. water (calcd. prior to exch.)	Expt.	Olson and Miller
33	5 → 2.2	Water	4.8	3.9	4.27	0.84	0.84	0.775	90	99
28	−0.9	7.9 *N* H_2SO_4	3.4	2.5	2.91	.79	.635	.315	26	24
29	− .04	1.1 *N* H_2SO_4	4.5	2.3	4.27	.79	.715	.625	84	..
40	14 → 13.7	1.0 *N* KOH	4.8	4.1	4.35	.85	.815	.225	4	2 (0.14 *N* NaOH)

only on the total rate of hydrolysis but also on the relative amount hydrolyzing by the different paths. Furthermore, they emphasized the fact that the agreement which they obtained between their experimental data in sulfuric acid solutions and the calculated results was due to their arbitrary selection of a *p*H value for these solutions. Later, unpublished work in this Laboratory by Dr. P. T. Youle has shown that acetate and formate ions also have specific effects on lactone hydrolysis, the acid ester possibly being formed as an intermediate. We, therefore, wish to restrict consideration to the hydrolysis in water and in potassium hydroxide solution in spite of the concordant results which we obtained in the sulfuric acid solutions.

Summary

β-Butyrolactone was hydrolyzed in heavy oxygen water to form β-hydroxybutyric acid. The potassium salt of the acid was decomposed by heating to form water and potassium crotonate. The water from the decomposition was then analyzed for isotopic oxygen content.

The results are in complete agreement with the mechanism of hydrolysis advanced by Olson and Miller, and are contradictory to the carbonium ion mechanism proposed by Rørdam.

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The Mechanism of the Photochemical Change of Acetylene[*]

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I. Introduction

Ultraviolet light of wave lengths smaller than 2350 Å. produces polymerization in gaseous acetylene. A considerable number of authors have investigated this reaction as well as the similar reaction which is sensitized by mercury vapor.[1–10]

In these investigations a number of facts have been established which may be summarized briefly. At room temperature the main product of the reaction is a yellow powder precipitated from the gas phase, which is of unknown structure and closely resembles cuprene. The reaction rate increases strongly with the temperature; above 270° the character of the reaction undergoes a change and a second solid is formed, a hard coating of dark yellow color, partly soluble in ether, not insoluble like cuprene. This second solid resembles the product of the purely thermal polymerization of acetylene.

The photochemical reaction proceeds proportional to the pressure of acetylene, at least at small pressures where the absorption is proportional to the pressure. At higher pressures the rate becomes constant, being dependent only on the intensity of the effective light, but during the process it is decreased gradually because of the light absorption by the reaction product precipitated from the gas phase onto the walls of the reaction vessel. Besides the solid product, a small amount of benzene is formed; its bands can be found in the absorption spectrum of the gas phase. Some of the additional bands found in the spectrum were attributed to naphthalene hydrocarbons. The absence of hydrogen and methane in the gas phase was confirmed by several authors, which result proves that acetylene is not decomposed, in this reaction, into hydrogen and carbon.

The reaction is generally assumed to proceed by a chain mechanism. Bates and Taylor[3] suggested, for the unsensitized reaction as well as for the mercury sensitized reaction, that the polymer is formed by the successive addition of acetylene molecules to one which has been activated. The chain length of the reaction had been found to vary with the temperature, from $n = 10$ at 20° to $n = 100$ at 250°, and it was found to depend neither on the light intensity nor on the pressure of acetylene.[10] There is little certain knowledge, however, about the

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