TABLE VI

PERCENTAGE COMPOSITION OF HYDROL

| | Monosacch. | Disacch. | Trisacch. | Water | Ash |
|---|---|---|---|---|---|
| | Hydrol | | | | |
| Mean (Table V) | 54.2 | 39.4 | 6.4 | .. | .. |
| Corrected mean | 55.2 | 38.4 | 6.4 | .. | .. |
| Whole analysis | 43.2 | 30.8 | 5.0 | 19.8 | 1.96 |
| | Reconverted Hydrol | | | | |
| Mean | 54.2 | 40.3 | 5.5 | .. | .. |
| Corrected mean | 55.2 | 39.3 | 5.5 | .. | .. |
| Whole analysis | 40.1 | 28.5 | 4.0 | 21.60 | 5.83 |
| | Kansas City Hydrol | | | | |
| Mean | 53.8 | 38.9 | 7.3 | .. | .. |
| Corrected mean | 54.8 | 37.9 | 7.3 | .. | .. |
| Whole analysis | 40.7 | 28.2 | 5.2 | 20.1 | 5.60 |

## Summary

A procedure has been developed for the direct analysis of sugar mixtures of these types: mono- and disaccharoses; mono-, di- and trisaccharoses; pentoses and hexoses. The procedure involves indirect methylation, vacuum distillation of the methylated derivatives, and weighing of the fractions thus obtained. An accuracy of 3% was attained. Since the various fractions are separated from each other, they may be used for purposes of identification.

The indirect methylation is necessary to obtain uniformity in yields. Direct methylation of a mixture of mono- and disaccharoses gives results in the fractional distillation which are not indicative of the original percentage composition. The following steps are involved in the standardized procedure: acetylation at 0° by acetic anhydride and pyridine, replacement of the acylal function by chlorine by means of titanium tetrachloride, substitution of the chlorine by methoxyl by prolonged shaking with methanol and silver carbonate, hydrolysis of the remaining acetyl groups by sodium methoxide in methanol, methylation by one treatment with methyl sulfate and sodium hydroxide, and finally fractional distillation *in vacuo* of the methylated sirups.

Monosaccharoses such as xylose, rhamnose, glucose and levoglucosan undergo the procedure successfully. In its present form it does not apply to fructose. The disaccharoses studied included the maltose type (maltose, lactose, gentiobiose) and the trehalose type (trehalose, sucrose).

The procedure has been applied to three types of hydrol and the presence of trisaccharoses in these hydrols has been established.

EVANSTON, ILLINOIS RECEIVED JULY 18, 1938

---

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

# The Mechanism of the Aqueous Hydrolysis of β-Butyrolactone

BY A. R. OLSON AND R. J. MILLER

In 1896 Walden[1] showed that *d*-malic acid was obtained when silver oxide was suspended in an aqueous solution of *d*-chlorosuccinic acid. Treatment of the chloro acid with potassium hydroxide yielded an *l*-malic acid. Holmberg[2] explained these results by assuming the primary formation of a lactone from the chloro acid, the lactone then hydrolyzing in several different ways, depending upon the hydrogen ion concentration. He[3] later succeeded in isolating the lactone. The generality of lactone formation from β-halogenated acids has been proved by Johansson's[4] work.

Holmberg[5] and Rørdam[6] studied the hydrolysis of the (+) malolactonic acid which was obtained from the (−) halogenosuccinic acids. They found that in dilute aqueous acids the hydrolysis was first order, and that the product contained a preponderance of (−) malic acid. In stronger acids, up to 2 *N* nitric acid and in basic solutions, the product was largely (+) malic acid. These results were confirmed and extended by Long and Olson,[7] who determined both rates and optical relations using buffered solutions. Their results are summarized in Figs. 1 and 2. The interpretation of these results is complicated by the difficulty of determining the total concentration of lactone and also by the possible existence of an α-lactone as well as a β-lactone. We have therefore turned to β-bromobutyric acid which readily yields a pure β-lactone. We have been able to show that this lactone hydrolyzes in neutral

---

(1) Walden, *Ber.*, **29**, 133 (1896).

(2) Holmberg, *ibid.*, **45**, 1713 (1922).

(3) Holmberg, *Svensk. Kem. Tids.*, **30**, 190 and 215 (1918), through *Chem. Zentr.*, **90**, I, 223 (1919).

(4) Johansson, *Lunds Universitets Årsskrift*, N. F., Part 2, **12**, No. 8 (1916).

(5) Holmberg, *J. prakt. Chem.*, **88**, 553 (1913).

(6) Rørdam, *J. Chem. Soc.*, **2**, 2931 (1932).

(7) Long and Olson, unpublished work in this Laboratory.

aqueous solution to yield one optical form of hydroxybutyric acid exclusively and reacts with hydrogen ion and hydroxide ion by two other mechanisms to form the other optical isomer.

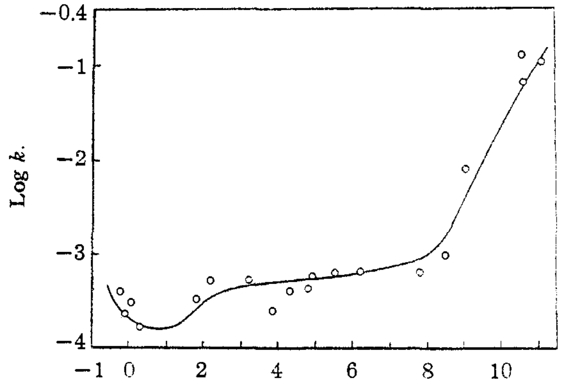


Fig. 1.—Velocity of hydrolysis of malolactonic acid.

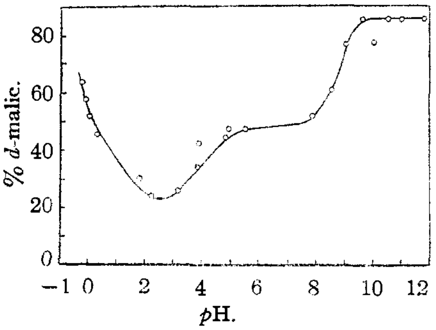


Fig. 2.—Optical form of malic acid produced by hydrolysis of (+) malolactonic acid.

The β-bromobutyric acid was prepared by Johansson's[8] method. The acid was resolved with morphine in methyl alcohol. Repeated recrystallization of the acid yielded a product which had a molar rotation of +116.5° in 2 *N* perchloric acid. This solution was 0.1632 *M* with respect to the β-bromobutyric acid. In water alone less than 1% decrease was observed. A 0.2361 *M* solution of the sodium salt had a molar rotation of 106.6°. The melting point of the purest acid was 44°. The β-butyrolactone was prepared from this acid by Johansson's procedure.

**Hydrolysis of the β-Butyrolactone.**—The lactone was weighed in volumetric flasks which then were filled to the mark with the solvent used for hydrolysis. The change of optical rotation with time and the final value reached were then observed using the polarimeter[9] described previously. This was a Bellingham and Stanley instrument designed so that 30-cm. polarimeter tubes in a thermostat with glass windows could be placed in the optical path. The thermostat was held at 25.0 ± 0.05° by means of a mercury regular and heaters. Light from a mercury lamp filtered through copper sulfate glass and a Wratten No. 77 filter was used for the readings with the Hg 5461 line. Unfiltered light from a sodium lamp was used for the sodium D lines. All readings were made to the nearest hundredth of a degree, and, except for the faster kinetic runs, the mean of six to ten readings was taken as an observation.

**Results and Discussion.**—It was known from the work of Johansson[4] that the hydrolysis of the lactone involves not only a first order reaction with water but also a second order reaction with hydroxide ion. In those solvents, therefore, where a change in the hydrogen ion concentration was apt to prove troublesome, we used buffers. In Table I we have collected the rate constants in various solvents. Those marked with an asterisk are copied from Johansson, who used a titration method for following the rate. In Fig. 3 we have plotted the rates which have been determined in this Laboratory, against the *p*H. For the 7.87 *N* sulfuric acid the activity of the hydrogen ion was taken arbitrarily as 7.87. The solid line in Figure 3 is the plot of the total rate at various hydrogen ion concentrations as calculated from the well-known equation for the catalytic catenary

$$-\mathrm{d}\,\log_e (\text{lactone})/\mathrm{d}t = k = k_{H_2O} + k_H(H^+) + k_{OH}(OH^-)$$

where $k_{H_2O}$ and $k_{OH}$ were determined by Johansson and $k_H$ was determined in 2 *N* perchloric acid.

Table I

Experimental Rates

| Solvent | Molar concn. of lactone | First order $k \times 10^4$ |
|---|---|---|
| 7.87 *N* $H_2SO_4$ | 0.288 | 72 |
| 2 *N* $HClO_4$ | .1685 | 12 |
| Water | .789 | 7 |
| 0.665 *M* $H_2PO_4^-$, 1.00 *M* $HPO_4^=$, *p*H 6.8 | .1890 | 29 |
| 0.60 *M* $HCO_3^-$, 2.18 *M* $CO_3^=$, *p*H 10 | .207 | 800 |
| Water* | .608 | 8.0 |
| Water* | .0600 | 8.8 |
| Water* | .00600 | 9.1 |
| 0.604 *M* $HNO_3$* | .603 | 9.2 |
| 0.0601 *M* $HNO_3$* | .0599 | 8.7 |
| 0.00600 *M* $HNO_3$* | .00600 | 9.0 |
| | | Second order |
| 0.00400 *M* NaOH* | .00400 | *C* = 49 |
| 0.00200 *M* NaOH* | .00200 | *C* = 49 |

---

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

[9] Olson and Long, This Journal, **56**, 1294 (1934).

The lack of agreement between some of our points and the solid line will be discussed in a later section in connection with salt effects. The details of the calculation of the solid line are found in Table II. The last column in the table is useful in connection with the discussion in a later section.

TABLE II

CALCULATED RATES

$$-\frac{\mathrm{d}\log_e[\text{lactone}]}{\mathrm{d}t} = k = k_{H_2O} + k_H(H^+) + k_{OH}(OH^-)$$

or $k = 8.5 \times 10^{-4} + 2 \times 10^{-4}(H^+) + 49(OH^-)$.

| $p$H | $k_H(H^+) \times 10^4$ | $k_{OH}(OH^-) \times 10^4$ | $k \times 10^4$ | $\frac{k_{H_2O}}{k} \times 100$ |
|---|---|---|---|---|
| − 2 | 200 | | 208.5 | 4.2 |
| − 1 | 20.0 | | 28.5 | 29.8 |
| − 0.5 | 6.3 | | 14.8 | 57.4 |
| 0 | 2.0 | | 10.5 | 81.0 |
| 1 | 0.2 | | 8.7 | 97.0 |
| 2 | .02 | | 8.52 | 99.7 |
| 3 | .002 | | 8.502 | 100.0 |
| 4 | | | 8.5 | 100.0 |
| 5 | | | 8.5 | 100.0 |
| 6 | | 0.0049 | 8.505 | 99.9 |
| 7 | | .049 | 8.55 | 99.4 |
| 8 | | .49 | 9.0 | 94.5 |
| 8.5 | | 1.5 | 10.0 | 85.0 |
| 9 | | 4.9 | 13.4 | 63.5 |
| 9.5 | | 15.0 | 23.5 | 36.0 |
| 10 | | 49.0 | 57.5 | 14.8 |
| 11 | | 490 | 498.5 | 1.7 |
| 12 | | 4900 | 4908.5 | 0.2 |

A change in the hydrogen ion concentration of the solvent in which the β-butyrolactone is hydrolyzed produces not only a change in the rate of hydrolysis as discussed above, but produces also a change in the ratio of the amount of (+) hydroxybutyric acid to the amount of (−) hydroxybutyric acid in the product. In order to determine this ratio the observed final rotation for each run must be corrected for the optical purity of the initial lactone. The corrected final rotation must then be compared with the molar rotation of pure hydroxybutyric acid in the same solvent. The correction was obtained by comparing the molar rotation of the bromobutyric acid from which the lactone was made with the rotation of the highly resolved bromobutyric acid. In Table III we enumerate the correction factors for the four preparations of bromobutyric acid which were used in this work. In Table IV we list the molar rotations of an optically impure sample of hydroxybutyric acid in the various solvents. Since the molar rotation of this sample of hydroxybutyric acid in water was only 18.5° we have multiplied all the experimentally determined molar rotations by a factor to obtain the rotation of pure hydroxybutyric acid. In Table V we have collected the data from the runs concerned with the optical form of the product. The first column indicates the preparation of bromobutyric acid from which the lactone was made, the second

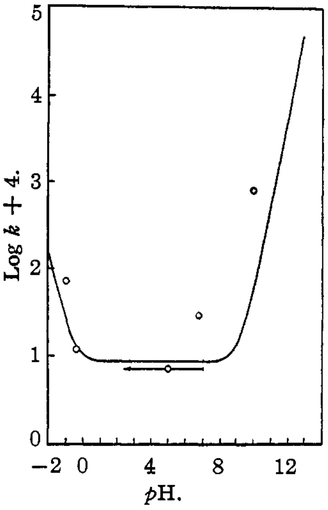


Fig. 3.—Rate of hydrolysis of β-butyrolactone.

TABLE III

| Prepn. of β-bromobutyric acid from which lactone was made | Molar rotation of this acid in 2 $N$ $HClO_4$ | 116.5 divided by this molar rotation or correction factor to rotation |
|---|---|---|
| I | 50.4 | 2.31 |
| II | 86.8 | 1.343 |
| III | 104.0 | 1.120 |
| IV | 100.7 | 1.158 |

TABLE IV

ROTATION[10] OF β-HYDROXYBUTYRIC ACID IN VARIOUS SOLVENTS

Free acid in aqueous solution, $[M]^{25}_D$ 25.9°. Sodium salt, $c$ = 0.13 $M$, $[M]^{25}_D$ 17.5° Hg 5461 calibration using 5 cc. of 0.789 $M$ acid solution of $[M]^{25}_D$ 18.5° diluted to 25 cc. with solvent, giving the concentration of β-hydroxybutyric acid = 0.789/5 = 0.1578 $M$ in all solvents except water where the original 0.789 $M$ solution was used.

| Solvent | $\alpha$ | $[M]^{25}_{5461}$ | $[M]^{25}_{5461} \times \frac{25.9}{18.5}$ |
|---|---|---|---|
| 7.87 $N$ $H_2SO_4$ | 1.12 | 23.6 | 33.1 |
| Acetate buffer $Ac^-$ = 0.8 $M$, HAc = 3.2 $M$, $p$H 3.85 | 1.03 | 21.7 | 30.4 |
| Water | 5.10 | 21.5 | 30.1 |
| Phosphate $p$H 6.8, 0.665 $M$ $H_2PO_4^-$, 1.0 $M$ $HPO_4^=$ | 0.77 | 16.2 | 22.7 |
| Carbonate $p$H 9, 2.00 $M$ $HCO_3^-$, 0.72 $M$ $CO_3^=$ | .77 | 16.2 | 22.7 |
| Carbonate $p$H 10, 0.6 $M$ $HCO_3^-$, 2.18 $M$ $CO_3^=$ | .76 | 16.0 | 22.4 |
| 6 $N$ NaOH | .62 | 13.1 | 18.4 |

---

[10] McKenzie, *J. Chem. Soc.*, **81**, 1402 (1902).

TABLE V

| Prepn. | Solvent | Initial molar concn. of lactone | Obsd. final rotation of soln. | $[M]^{25}_{5461}$ | Corrected $[M]^{25}_{5461}$ | Rotation of pure β-hydroxybutyric acid in solvent | Corrected [M] × 100 divided by rotation of pure hydroxybutyric acid | Per cent. (+) form |
|---|---|---|---|---|---|---|---|---|
| I | 7.87 *N* $H_2SO_4$ | 0.288 | −0.65 | − 7.5 | −17.3 | 33.1 | −52 | 24 |
| III | 2 *N* $HClO_4$ | .1685 | .13 | 2.6 | 2.9 | (30.1)[a] | 10 | 55 |
| I | Formate buffer, *p*H 2.8 | .363 | 1.36 | 12.5 | 28.8 | (30.1)[a] | 96 | 98 |
| III | Acetate buffer, HAc = 3.2 *M*, Ac = 0.8 *M*, *p*H 3.8 | .1319 | 1.02 | 27.0 | 30.2 | 30.6 | 98.7 | 99.4 |
| I | Water | .113 | 0.40 | 11.8 | 27.0 | 30.1 | 90 | 95 |
| II | Water | .789 | 5.10 | 21.5 | 28.9 | 30.1 | 96 | 98 |
| | | | 4.37[b] | 18.5 | 24.8 | 25.9 | 96 | 98 |
| III | Water | .1932 | 1.54 | 26.4 | 29.7 | 30.1 | 98.7 | 99.3 |
| | | | 1.32[b] | 22.7 | 25.4 | 25.9 | 98.0 | 99.0 |
| III | 0.665 *M* $H_2PO_4^-$, 1.0 *M* $HPO_4^{=}$, *p*H 6.8 | .1890 | 1.14 | 20.0 | 22.4 | 22.7 | 98.6 | 99.3 |
| I | 2.00 *M* $HCO_3^-$, 0.72 *M* $CO_3^{=}$, *p*H 9 | .118 | 0.00 | 0.0 | 0.0 | 22.7 | 0 | 50 |
| III | 0.60 *M* $HCO_3^-$, 2.18 *M* $CO_3^{=}$, *p*H 10 | .207 | − .40 | − 6.4 | − 7.2 | 22.4 | −32 | 34 |
| III | 0.140 *M* NaOH | .140 | − .63[b] | −15.0 | −16.8 | 17.5 | −96 | 2 |
| I | 6 *N* NaOH | .308 | − .65 | − 7.0 | −16.1 | 18.4 | −88 | 6 |
| IV | 6 *N* NaOH | .249 | −1.07 | −14.3 | −16.5 | 18.4 | −90 | 5 |

[a] In the absence of experimental data rotation in water was used.

[b] Indicates runs made with sodium light.

the solvent in which the lactone was hydrolyzed, the third the initial molar concentration of lactone, and the fourth was observed final rotation. The percentages of (+) hydroxybutyric acid in the product as calculated from the corrected rotations are shown in the last column of Table V and plotted against the *p*H in Fig. 4. Where an unbuffered solution was used an arrow shows the change in *p*H during hydrolysis.

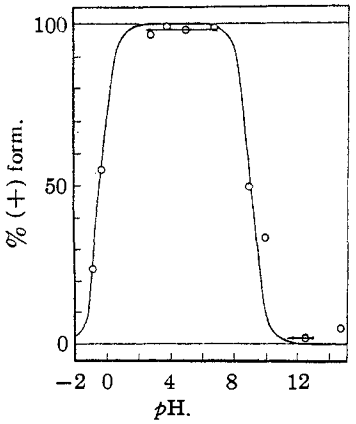


Fig. 4.—Optical form of hydroxybutyric acid produced by the hydrolysis of (+) β-butyrolactone.

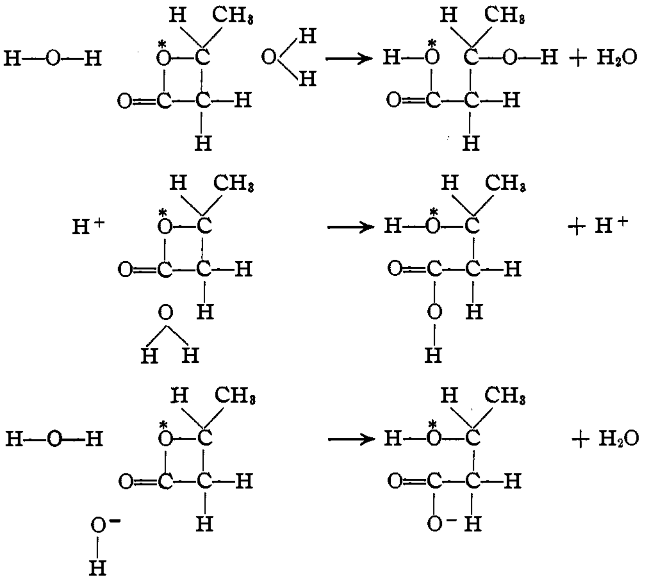
If we assume that (+) β-butyrolactone reacts with water molecules to form only (+) hydroxybutyric acid and with hydrogen ions or hydroxyl ions to form only (−) hydroxybutyric acid, and if we combine these assumptions with the rates as determined in the preceding sections, we can calculate the percentage of (+) hydroxybutyric acid formed in the various solvents. This we have done with the aid of the last column in Table II and have plotted the results as the solid line in Fig. 4. The agreement between the experimental and calculated percentages is quite satisfactory except for the point at *p*H of 10 and the point in 6 *N* sodium hydroxide. The agreement for the point corresponding to 7.87 *N* sulfuric acid is of course due to our arbitrary selection of an activity for the hydrogen ion. If we had calculated the activity from the mean activity rule of Lewis and Randall,[11] the point would have come to the right of that for 2 *N* perchloric acid. This procedure of course neglects a specific contribution to the rate by the acid sulfate ion. That this ion contributes to the rate is made very plausible by the work to be discussed later in connection with carbonate ion.

The low rotation in the 6 *N* sodium hydroxide may be due to reactions producing unsaturated compounds such as is observed with bromobutyric acid in alkaline solutions.

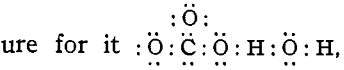
---

[11] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, pp. 328 and 357.

Postponing for the present the discussion of the point at *p*H 10, we can conclude that the composite reaction is the resultant of the three reactions.



These reactions are written in conformity with the principle that inversion occurs for every substitution. The formation of the lactone from the bromobutyric acid must have involved an inversion even though there is no change in rotation, for the action of phosphorus pentachloride on (−) hydroxybutyric acid or its ester produces a (+) chlorobutyric acid[12] or its ester, respectively. It is of interest to recall in this connection that (+) bromosuccinic acid produces a lactone with negative rotation. The lactone is in reality an inner ester. The breaking of the carboxyl oxygen bond under acid or alkaline conditions is in agreement with the hydrolysis of esters under similar conditions.[13] The hydrolysis of the lactone by molecular water is fast enough to be observed. In this case it is the alcohol oxygen bond which is broken. Due to the fact that we used optically active materials, we see that the big speeding up of the reaction by hydrogen ions and hydroxyl ions therefore does not necessarily involve a catalysis of the water reaction, but rather the acceleration of independent, competing reactions. In view of these results we must disagree with Waters,[14] who states "Without exception hydrolyses are ionic reactions..."

In Fig. 3 the point corresponding to the hydrolysis of a 0.789 *M* solution of the lactone in pure water shows a slower rate than that calculated for a 0.15 *M* solution. This is in agreement with Johansson's work in which it was found that the first order rate constants decreased as the concentration of the lactone increased. We already have mentioned the difficulty of assigning an activity to the hydrogen ion in the 7.87 *N* sulfuric acid. In addition to this the rate also should deviate from that calculated for a dilute solution due to the changes of the activity of water and of lactone as we go to such a concentrated solution. These effects are likewise very prominent in the runs with phosphate and carbonate buffers where the salt concentrations are several moles per liter. Thus the velocity of the run in the phosphate solution is about three times the calculated rate. A distribution experiment using dibutyl ether as the second solvent showed that the activity of the lactone in the phosphate solution was about twice as great as it was in water solution, accounting for the major portion of the rate change. The run in the carbonate buffer cannot be explained in this way, for here we get not only a thirteen-fold increase in the composite rate but also a change in the optical ratio of the product. This ratio would not be changed by a change in the activity of the lactone. Therefore, even after allowing for a two-fold change in the activity of the lactone by the salt, we find a five-fold increase in the rate of the reaction with hydroxide ion and fifteen-fold increase in the water reaction rate. If we think of the carbonate ion in solution as hydrated and write a structure for it  $:\underset{..}{\ddot{O}}:\overset{:\ddot{O}:}{\underset{..}{\dot{C}}}:\underset{..}{\ddot{O}}:H:\underset{..}{\ddot{O}}:H$, we see that the water in this complex is intermediate between molecular water and hydroxide ion since the hydrogen which forms the bond is no longer completely the property of the water. Assuming that the behavior of such a particle is intermediate between that of hydroxide ion and molecular water, we would expect the observed changes in the rates and products.

**Reactions of β-Bromobutyric Acid.**—The disappearance of β-bromobutyrate ion in aqueous solution at 25° gave a first order rate constant of $1.09 \times 10^{-3}$ min.$^{-1}$. Runs which were followed by Volhard titration or by change of optical rotation gave identical results. The rate of this re-

---

(12) Fischer and Scheibler, *Ber.*, **42**, 1219 (1909).

(13) (a) Holmberg, *ibid.*, **45**, 2997 (1912), and (b) Polanyi and Szabo, *Trans. Faraday Soc.*, **30**, 508 (1934).

(14) Waters, "Physical Aspects of Organic Chemistry," Routledge and Sons, Ltd., London, p. 262.

action at 38° was found by Johansson[8] to be 0.0093. Combining these results we get $k = 1.3 \times 10^{17}e^{-29,800/RT}\text{sec.}^{-1}$. Later Johansson[15] found that at 32° about 15% of the β-bromobutyrate decomposed into propylene, carbon dioxide, and bromide ion. At 25° we found a 17% discrepancy between the production of bromide ion and of acid after the hydrolysis of sodium β-bromobutyrate was complete, indicating about the same amount of decomposition. If all of the hydrolysis of the sodium bromobutyrate proceeds through the lactone intermediate, the optical activity of the product should be the same as that which is obtained from the hydrolysis of the lactone. Correcting for the 15% decomposition reaction this was found to be the case.

An aqueous solution of sodium bromobutyrate and thiosulfate ion shows an induction period when the rate is followed by titration of the thiosulfate ion. The induction period becomes shorter the greater the initial concentration of thiosulfate ion. The limiting value for the rate appears to be the same as the rate of production of bromide ion when thiosulfate ion is absent. The reaction therefore probably involves the preliminary production of lactone and bromide ion. In corroboration of this, the rate of the bimolecular reaction between lactone and thiosulfate ion was determined by following the change in concentration of thiosulfate ion and found to be 0.05 liter per mole-minute. The results therefore are completely analogous to those obtained by Long and Olson[16] with sodium bromosuccinate.

In solution by itself or with 2 $N$ perchloric acid the β-bromobutyric acid loses its optical activity only very slowly, the rotation in 2 $N$ perchloric acid being 55% of the beginning rotation after two months at 25°. In basic solution, however, a fast bimolecular reaction with hydroxide ion occurs, producing an optically inactive substance, probably crotonate ion, such as Fischer and Scheibler[12] found with sodium β-chlorobutyrate. The rate constant as determined by the decrease in optical activity with time was about 0.08 liter per mole-minute at 25°.

The racemization by bromide ion was followed in approximately 0.2 $N$ β-bromobutyric acid and 2 $N$ hydrobromic acid by the decrease in optical activity. The rate constants, uncorrected for decrease in optical activity due to other causes, since this correction was small and known only in the case of the lower temperature, were $1.27 \times 10^{-5}$ minute$^{-1}$ at 25° and $9.2 \times 10^{-5}$ minute$^{-1}$ at 39.3° as the results of a single run at each temperature. The rate constant can then be expressed as $k = 4.2 \times 10^{11}e^{-24,900/RT}\text{sec.}^{-1}$ as a preliminary result.

## Summary

Pure optically active β-bromobutyric acid has been prepared. Its molar rotation, $[M]^{25}_{5461}$, in acid solution is 116.5°. In aqueous solution the salt gave $[M]^{25}_{5461}$ equal to 106.6°.

The rates of hydrolysis of optically active β-butyrolactone prepared from optically active β-bromobutyric acid have been measured over a range of hydrogen ion concentrations.

From the rates and the optical activity of the final hydrolysis products it has been shown that the mechanisms of hydrolysis by water, by hydrogen ion, and by hydroxide ion are distinct.

It has been shown that the addition of an ion, such as carbonate ion, has a big influence on both the water rate and the hydroxide ion rate. An explanation is advanced for this behavior.

Tentative values of the heats of activation for the reaction by which β-bromobutyrate ion produces lactone and for the reaction by which bromide ion racemizes β-bromobutyric acid have been determined.

The rate of the bimolecular reaction between β-bromobutyrate ion and hydroxide ion was determined to be about 0.08 liter per mole-minute.

The reaction between β-bromobutyrate ion and thiosulfate ion has been shown to involve the unimolecular formation of lactone as a primary step.

BERKELEY, CALIF. RECEIVED JULY 15, 1938

---

(15) Johansson, *Ber.*, **55**, 647 (1922).

(16) Long and Olson, *J. Phys. Chem.*, **41**, 267 (1937).