[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA]

The Hydrolysis of β-Butyrolactone[1]

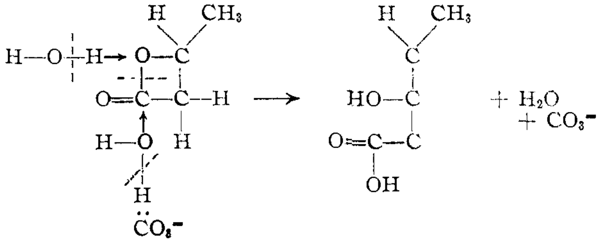
BY A. R. OLSON AND P. V. YOULE[1a]

Previous work has shown that at least two mechanisms are involved in the hydrolysis of β-butyrolactone producing the two optical forms of β-hydroxybutyric acid. The work is here extended so as to permit a determination of two catalytic coefficients for each of the following bases: carbonate ions, phosphate ions and tetraborate ions. The separate catalytic coefficients, but not their sums, fit Brønsted diagrams. It is suggested that the occurrence of simultaneous multiple reactions may contribute to the curvature that has been observed in the Brønsted diagrams of other reactions.

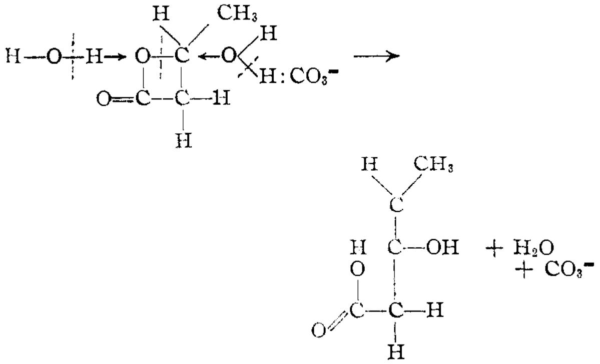
β-Butyrolactone reacts with water and its ions to form hydroxybutyric acid. The rate of hydrolysis can be expressed by the equation

$$\frac{d \ln (\text{lactone})}{dt} = k_{H_2O} + k_1(H^+) + k_2(OH^-) \quad (1)$$

If the solution contains ions of weak acids or bases, a fourth term (which may be complex) must be added to (1). By employing optically active lactone, Olson and Miller[2] were able to show that the reaction with molecular water produced only that acid that rotates the plane of polarized light in the same direction as did the original lactone a reaction that involves an inversion of the alcoholic carbon and that the reactions involving either H^+ or OH^- produced only the enantiomorph. They further showed that a base like $CO_3^=$ produced a mixture of the two optical forms. In postulating mechanisms for these reactions, they found it necessary to assume that a molecule of water is involved, in addition to each reactant specifically indicated in the terms in the right hand side of equation (1), resulting in reactions now familiarly known as "push-pull" reactions. For carbonate ions the results can be represented as



and



These results were confirmed[3] by hydrolyzing the lactone in heavy oxygen water, decomposing the product and analyzing the water formed by the decomposition for isotopic oxygen content by the method of Cohn and Urey.[4]

According to Brønsted the specific velocity constant (k_a, k_b) for an acidic or basic catalyst is related to the acid or base constant (K_a, K_b) of the catalyst by the equation

$$k_{a,b} = GK^x_{a,b}$$

where G and x are empirical constants. Following Brønsted and Pedersen,[5] many investigators have obtained data in agreement with this equation. However, Olson and Miller found that that portion of the rate corresponding to catalysis by carbonate ion was complex. We address ourselves therefor to the questions: (1) Are the reactions involving other basic catalysts similarly complex? (2) For any one catalyst does the Brønsted relationship apply to the over-all reaction or to its separate parts?

The study of the hydrolysis of β-butyrolactone might be complicated by (1) regeneration of lactone from hydroxybutyric acid, (2) decomposition of hydroxybutyric acid into water and crotonic acid or into propylene and carbon dioxide, (3) ester formation with organic bases. Within the limits of error the titration results in Table I show the hydrolysis to be irreversible. The data of Pressman and Lucas[6] indicate that the second reaction should be unimportant near room temperature. However, some of our results, particularly those at 35°, are marred by interfering reactions. Ester formation with organic anion bases is important. It will be discussed in a subsequent paragraph.

The preparation of optically active β-butyrolactone and the study of its hydrolysis by polarimetric experiments, followed exactly the procedure outlined by Olson and Miller. In those experiments where the reaction was followed by titrations, carbon dioxide was excluded from the reaction and titration vessels by sweeping them out with a stream of purified nitrogen. The reaction with water was unimolecular and the reaction with hydroxide ion bimolecular over its whole course. For the rapid hydroxide ion reaction, 200 cc. of CO_2-free water was placed in a stoppered bottle containing a handful of glass beads. An ampoule containing a weighed amount of lactone was added and then an amount of barium hy-

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[1] The work that is reported in this article was performed over ten years ago. Its publication has been delayed partly by the war and partly by the hope that more complete and more precise data would be obtained. Since this hope has not been realized, the material is now being released.

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[2] A. R. Olson and R. J. Miller, THIS JOURNAL, **60**, 2687 (1938).

[3] A. R. Olson and L. J. Hyde, *ibid.*, **63**, 2459 (1941).

[4] Mildred Cohn and H. C. Urey, *ibid.*, **60**, 679 (1938).

[5] J. N. Brønsted and K. Pedersen, *Z. physik. Chem.*, **108**, 185 (1924).

[6] D. Pressman and H. J. Lucas, THIS JOURNAL, **61**, 2271 (1939).

droxide equivalent to this amount of lactone. The reaction could be started at a given instant by shaking the bottle. At appropriate intervals 50 cc. of the mixture was added to a known quantity of 0.1 *N* acid to stop the reaction. Titration with barium hydroxide solution gave the amount of lactone decomposed. The results are summarized in Table I.

TABLE I

HYDROLYSIS BY WATER

(a) Typical titration: initial concentration of lactone 0.0185 *M*, temp., 20°

Minutes	Ml. 0.104 *N* $Ba(OH)_2$	$k \times 10^4$
400	1.52	4.69
1271	3.81	4.38

(b) Summary of rates and activation energies

Temp., °C.	$k \times 10^4$	*E*
20	4.6	
25	8.2	20.8
30	14.4	19.8
35	24.8	19.7

TABLE II

HYDROLYSIS BY HYDROXIDE ION

(a) Typical titration: initial concentration of lactone and of OH^- 6.6 × 10^{-3} *M*, temp., 20°

Minutes	Ml. 0.1 *N* HCl	Ml. 0.104 *N* $Ba(OH)_2$	*k*
5	1.70	0.17	35.3
10	1.20	.18	34.2
15	0.90	.15	34.8

(b) Summary of rates and activation energies

Temp., °C.	*k*	*E*
20	35.0	13.3
25	51.2	12.6
30	72.5	7.7
35	90	

In Table IIIa we have summarized the data for a group of experiments in carbonate buffer solutions at 25°. In this table, the quantities in the second, third and fourth columns are properties of the buffers, *C* is the initial molal concentration of the lactone, *k* is the total first order rate constant, α is the final rotation of the solution, and *R* is the factor by which the rotation should be multiplied due to the fact that the lactone was prepared from an optically impure acid. The change in rotation as the lactone hydrolyzes is not large. Furthermore, emulsion formation limits the concentration of lactone. These factors operate to decrease the precision of *k* as well as α.

TABLE IIIa

Buffer	*M* $CO_3^=$	*M* HCO_3^-	*p*H	*C*	$k \times 10^4$	α	*R*
1	2.18	0.60	10.0	0.207	749	−0.40	1.12
2	1.46	0.40	10.0	.0485	529	− .05	1.72
3	1.09	0.30	10.0	.0690	426	− .09	1.72
4	0.72	2.00	9.4	.0876	259	− .065	1.72
5_1	0.20	2.48	8.5	.0412	80	− .01	1.72
5_2	0.20	2.48	8.5	.125	70	+ .04	1.72

TABLE IIIb

Buffer	(*M*)	$(M)_{cor.}$	*p*	$k_{H_2O} \times 10^4$	$k_{OH}(OH^-) \times 10^4$
1	−6.45	−7.23	0.34	8.5	49
2	−3.44	−5.95	.365	8.5	49
3	−4.35	−7.50	.33	8.5	49
4	−2.50	−4.25	.405	8.5	12
5_1	− .81	−1.39	.47	8.5	1.5
5_2	+1.07	+1.84	.54	8.5	1.5

Table IIIb is a continuation of Table IIIa. (*M*) is the molal rotation calculated from α, $(M)_{cor.}$ is obtained from (*M*) by applying *R*. The molal rotation of optically pure β-hydroxybutyric acid, $M_{100\%}$, in these buffers is 22.4°. The ratio of (*M*) to $M_{100\%}$ gives *p*, the fraction (+) acid in the product. If *k* in Table IIIa is multiplied by *p*, we obtain the total (+) rate. Since water contributes to the (+) rate and OH^- to the (−) rate, we subtract the values in the last two columns in Table IIIb to obtain the (+) and (−) contributions of the anions.

By varying the relative proportions of bicarbonate and carbonate ions, the catalytic contributions for each should be obtained. Actually no contribution from bicarbonate ion could be detected, carbonic acid being a stronger acid and bicarbonate ion a weaker base than the usually quoted ionization constant indicates.[7] Consequently to the carbonate ion present were ascribed plus and minus rate contributions, $(k^{+}_{CO_3})(CO_3^{=})$ and $(k^{-}_{CO_3})(CO_3^{=})$, from which the plus and minus specific catalytic coefficients can be calculated. In Table IIIc we have collected these calculations:

TABLE IIIc

All rate constants have been multiplied by 10^4

Buffer	k^+	$k^{-}_{CO_3}(CO_3^{=})$	$k^{+}_{CO_3}(CO_3^{=})$	$k^{-}_{CO_3}$	$k^{+}_{CO_3}$	k_{CO_3}
1	255	445	246	208	112	320
2	193	287	184	197	126	323
3	141	236	132	216	121	337
4	105	142	97	197	135	332
$5_{av.}$	38	35.5	29.5	178	148	326
			Av.	199	128	328

The total catalytic coefficient for $CO_3^=$ is surprisingly constant. Throughout this work we have neglected salt effects as well as any catalysis or ester formation by the hydroxybutyrate ion.

In Table IV we have collected the experimental data, and in Table V, the calculations, relating to experiments with carbonate buffers at 30 and 35°, as well as experiments using phosphate and borax buffers at all three temperatures. The calculations follow the pattern presented in detail for the car-

TABLE IV

EXPERIMENTAL RESULTS AT OTHER TEMPERATURES AND IN OTHER INORGANIC BUFFERS

Temp., °C.	Buffer	*p*H	Lactone, *M*	$k \times 10^4$	Plus form, %
30	0.545 *M* $CO_3^=$	10	0.0975	360	25
	.15 *M* HCO_3^-	10			
30	.545 *M* $CO_3^=$	10	.066	416	25
35	.15 *M* HCO_3^-	10	.0827	595	19
25	.50 *M* $HPO_4^=$	7	.145	26.4	88.5
	.33 *M* $H_2PO_4^-$				
30	0.50 *M* HPO_4	7	.117	46.2	85
35	0.33 *M* $H_2PO_4^-$	7	.124	80.8	90
25	.10 *M* $Na_2B_4O_7$	9.3–8.4	.0805	29.6	55
30	.10 *M* $Na_2B_4O_7$	9.3–8.4	.118	60.0	47

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(7) A. R. Olson and P. V. Youle, THIS JOURNAL, **62**, 1027 (1940).

Table V

Specific Rate Constants × 10^5

Temp., °C.	Base	(k_b)	(k_b^+)	(k_b^-)
25	$CO_3^=$	328	128	200
30 av.	$CO_3^=$	552	150	402
35	$CO_3^=$	880	162	718
25	$HPO_4^=$	36	30	6
30	$HPO_4^=$	63	49	14
35	$HPO_4^=$	112	96	16
25	$B_4O_7^=$	160	78	82
30	$B_4O_7^=$	298	140	158

bonate buffer solutions at 25°. The probable occurrence of interfering reactions at the higher temperatures has been mentioned. With phosphate buffers the reaction mixture became brownish and slightly opaque. Usually concentrated solutions were used to maintain the pH. In the borax buffer solutions the pH was measured and the OH^- contribution to the rate was calculated from the mean pH.

In Table VI the parameters of the Arrhenius equation have been collected. Obviously these quantities involve rather large uncertainties.

Table VI

Parameters of the Arrhenius Equation for the 25–30° Interval

Catalyst or reactant		log k_b	log A (sec.)	E(kcal./mole)
H_2O	+	− 1.7	8	20
OH^-	−	15.7	13.5	13
$CO_3^=$	+	10.3	0.7	6
$CO_3^=$	−		15	25
$HPO_4^=$	+	7.2	8.2	17
$HPO_4^=$	−		17.1	30
$B_4O_7^=$	+	9.3	11.6	21
$B_4O_7^=$	−		13.8	24

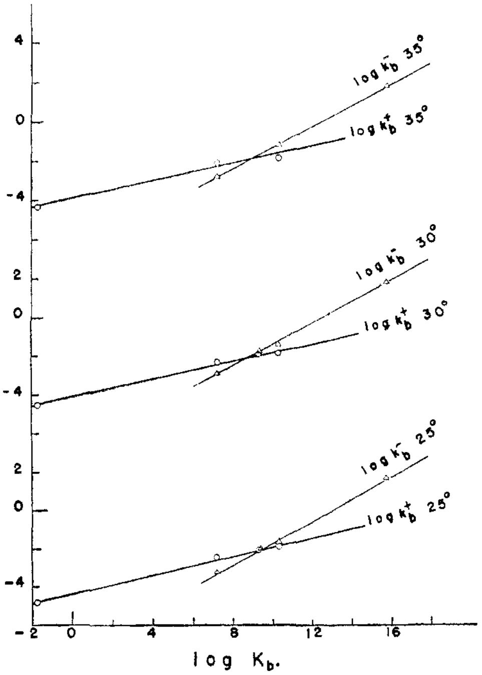


Fig. 1.—Variation of the specific rate constants of lactone hydrolysis with base strength of catalyst ions.

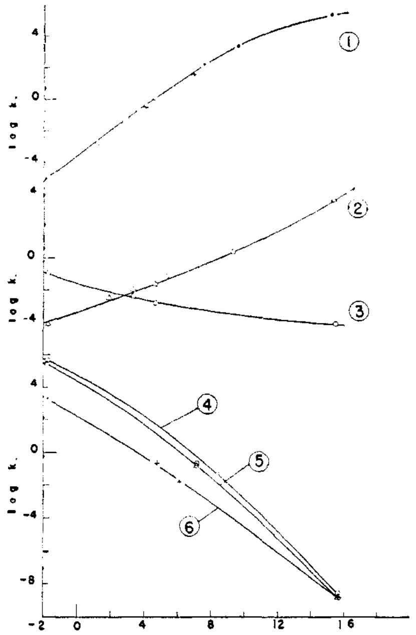


Fig. 2.—Variation of the specific rate constants with acid or base strength of catalysts: (1) the nitramide decomposition: O, data from E. C. Baughan and R. P. Bell, *Proc. Roy Soc.* (*London*), **158**, 464 (1937); ×, data from L. K. J. Tong and A. R. Olson, This Journal, **63**, 3406 (1941). (2, 3) the mutarotation of glucose: (2) acid catalyzed; (3) base catalyzed; data from J. N. Brønsted and E. A. Guggenheim, *ibid.*, **49**, 2554 (1927). (4, 5, 6) the hydrolysis of ethyl ortho esters; data from J. N. Brønsted and W. F. K. Wynn-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

A typical Brønsted diagram in which log k_b is plotted against log K_b yields a curve. However,

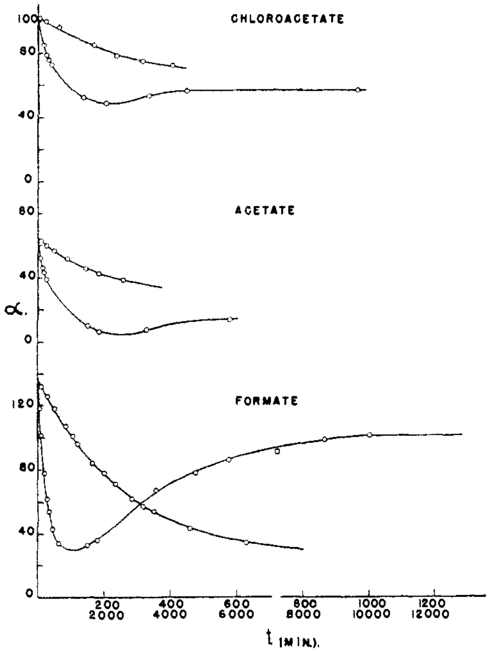


Fig. 3.—Rotational changes produced in lactone solutions by ions of organic acids. The upper time scale refers to the upper curve in each set.

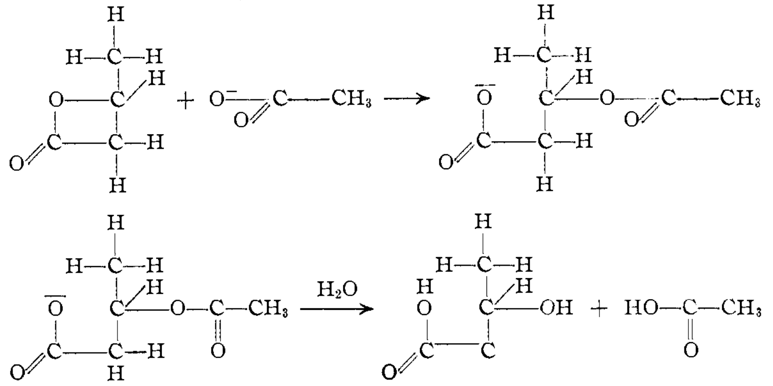
if $\log k_b^+$ and $\log k_b^-$ are plotted against $\log K_b$, the data for a single temperature fall fairly well on two straight lines as shown in Fig. 1. No corrections for statistical factors have been used.

In Fig. 2 we have plotted $\log k$ against $\log K$ for the reactions: (1) The nitramide decomposition,[8] (2) the mutarotation of glucose,[9] (3) the hydrolysis of ethyl ortho esters.[10] There is an arithmetical error in the value given by these authors for k_{H_2O}.

The authors of the articles usually have pointed out that graphs of this type show curvature. Thus Brønsted and Pedersen stated clearly theoretical reasons for believing that k must approach a maximum value asymptotically as K increases. For the nitramide decomposition, this was found experimentally by Tong and Olson. The present results show that in the lactone hydrolysis, the catalytic ability of a base like $CO_3^=$ must be expressed as due not to one but to two catalytic coefficients. Figure 1 demonstrates that each of these coefficients separately is compatible with an equation of the Brønsted type. Unless there is a constant proportionality between the coefficients for all catalysts, the plot of $\log(k^+ + k^-)$ against $\log K$ will not be linear.

The similarity between the lactone reactions and some of the others that have been studied, suggests that simultaneous multiple reactions may contribute to the curvatures that have been noticed in the Brønsted diagrams. Indeed the existence of at least two reactions has been demonstrated in the esterification of alcohols by thiol acids.[11]

When formate, acetate or chloroacetate buffers are used as media for the hydrolysis of β-butyrolactone, the optical rotation of the solution first decreases and then increases (Fig. 3). It is obvious that the ester which is formed hydrolyzes so slowly that the measured rotation no longer can be regarded as the resultant of the rotations of the lactone and the hydroxy butyric acids. Additional data therefore are needed for an analysis of the problem. The mechanism involved probably is



since the same optical form of hydroxybutyric acid is obtained as in hydrolysis by neutral water.

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[8] E. C. Baughn and R. P. Bell, *Proc. Roy. Soc.* (*London*), **158**, 464 (1937); L. K. J. Tong and A. R. Olson, THIS JOURNAL, **63**, 3406 (1941).

[9] J. N. Brønsted and E. A. Guggenheim, *ibid.*, **49**, 2554 (1927).

[10] J. N. Brønsted and W. F. K. Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).

[11] L. S. Pratt and E. E. Reid, THIS JOURNAL, **37**, 1934 (1915); F. B. Stewart and P. V. McKinney, *ibid.*, **53**, 1482 (1931).

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF OAK RIDGE NATIONAL LABORATORY]

C^{14} Tracer Studies in the Rearrangement of Unsymmetrical α-Diketones. II.[1] The Alkaline Rearrangement of Benzylideneacetophenone Oxide[2,3]

BY CLAIR J. COLLINS AND O. KENTON NEVILLE

Benzylideneacetophenone oxide, labeled with carbon-14 in the carbonyl group, has been found to form 2-hydroxy-2,3-diphenylpropionic acid labeled exclusively in the carbinol group. The results are in accord with a formulation involving the benzyl-group migration of the intermediate benzyl phenyl diketone.

Benzylideneacetophenone oxide (I) undergoes rearrangement in alcoholic alkali to yield 2-hydroxy-2,3-diphenylpropionic acid (V).[4]

The rearrangement, which has been of interest as a preparative method for certain unsymmetrical desoxybenzoins,[5] has been assumed[4,5b] to occur by a benzilic-acid type of rearrangement of the intermediate benzyl phenyl diketone (II), which can be isolated after short treatment of the epoxide with alcoholic alkali.

Since the α-diketone (II) is unsymmetrical, two possible ionic intermediates may be formulated[1]; one (III), which yields the rearranged product by benzyl-group migration, and the other (IV), in which a shift of the phenyl group must occur.[6]

The identity of the migrating group has been established by the use of carbon-14 as the labeling atom in the reaction series shown below. The radioactivities, reported in microcuries per millimole, were obtained by ion-chamber measurements of the

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[1] Paper I in this series, O. K. Neville, THIS JOURNAL, **70**, 3499 (1948).

[2] This document is based on work performed for the Atomic Energy Commission at Oak Ridge National Laboratory.

[3] Presented before the Division of Organic Chemistry at the 114th Meeting of the American Chemical Society, St. Louis, Missouri, September 7, 1948.

[4] O. Widman, *Ber.*, **49**, 477 (1916).

[5] (a) H. Jorlander, *ibid.*, **50**, 406, 1457 (1917); (b) W. Baker and R. Robinson, *J. Chem. Soc.*, 1798 (1932); (c) R. P. Dodwadmath and T. S. Wheeler, *Proc. Ind. Acad. Sci.*, 2438 (1935); (d) W. A. Hutchins, D. C. Motwani, K. D. Mudbhatkal and T. S. Wheeler, *J. Chem. Soc.*, 1882 (1938).

[6] T. Malkin and R. J. Robinson, *ibid.*, 371 (1925), have shown that benzyl phenyl diketone rearranges faster than benzil and, therefore, have concluded that the reaction proceeds by benzyl-group migration.