

and Miss Jean Thomas of the University of Wisconsin for further details concerning construction and manipulation of their optical system and diffusion cell. Our thanks are also due to Mr. Stanley Cassid, instrument maker, for many helpful suggestions and for his careful construction of our diffusion cell.

### Summary

1. The diffusion coefficient of sucrose in highly concentrated and supersaturated solutions has been measured at 25 and 35° by two optical methods, the usual schlieren method and the new Gouy interference-fringe method. The latter

method gave more accurate results from the standpoint of internal consistency and on an absolute basis also, we believe.

2. A new diffusion cell is described.

3. The diffusion coefficients decrease linearly with increase in weight per cent. of sucrose extrapolating to zero at 81% sugar at both temperatures, but they are all higher by 5–10 fold than diffusion coefficients calculated from Gordon's equation. We believe this to be due to a possible difference in mechanism between the viscous flow and diffusion processes as the solution becomes highly concentrated.

EVANSTON, ILLINOIS

RECEIVED OCTOBER 10, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

## The Kinetics of Hydrolysis of $\beta$ -Propiolactone in Acid, Neutral and Basic Solutions<sup>1</sup>

BY F. A. LONG AND MARY PURCHASE

The hydrolysis of lactones to give hydroxy acids is usually considered to be a typical case of ester hydrolysis. This appears to be valid for  $\gamma$ -lactones which give the expected hydroxide ion and acid catalyzed reactions. However with  $\beta$ -lactones an added reaction with water enters.<sup>2</sup> With  $\beta$ -butyrolactone Olson and co-workers<sup>3,4</sup> have shown that the hydrolysis in basic and in strongly acid solutions results in the expected acyl-oxygen fission and retention of configuration of the  $\beta$ -carbon. However, in the pH range of from 1 to 7 the only observable reaction is a pH independent hydrolysis which splits the alkyl-oxygen bond and inverts the configuration of the  $\beta$ -carbon.

Since Olson and co-workers were primarily interested in the mechanisms of the hydrolysis of  $\beta$ -butyrolactone they did not investigate the kinetics very fully. This is particularly true of the acid catalyzed reaction. Consequently we have investigated the hydrolysis of the related  $\beta$ -propiolactone in acid, basic and neutral solutions with emphasis on the temperature coefficients of the reactions and on the kinetics of the acid catalyzed reaction. The reactions of  $\beta$ -propiolactone with hydroxide ion and water have been studied at 25° by Johansson<sup>2</sup>; the acid catalyzed hydrolysis has not been previously investigated.

**Materials and Procedures.**—The  $\beta$ -propiolactone used in these studies was obtained from the B. F. Goodrich Chemical Company. It was stored at 5° and from 30 to 50 ml. were redistilled at reduced pressure from time to time. Its freezing point was found to be  $-33.4^\circ$ . Its equivalent weight was determined by addition of excess base

and back titration with acid and was found to be 71.93, indicating a purity of 99.8% or better.

Since the  $\beta$ -propiolactone has a marked tendency to polymerize,<sup>5</sup> preliminary tests were made to see if this would complicate the hydrolysis experiments. It was concluded that in the dilute (not over 0.1 molar) aqueous solutions used in these studies, the polymerization was too slow to be of any consequence.

The study of the bimolecular reaction of the  $\beta$ -lactone with hydroxide ion was followed by a conductivity method similar to that used by Hegen and Wolfenden.<sup>6</sup> The cells were typical conductivity cells with platinized platinum electrodes. They were kept at constant temperature by using a regulated oil-bath. The conductivity bridge was a somewhat simplified version of the Jones bridge. All conductivity studies were made with carbon dioxide-free solutions.

The equation used to calculate the rate constant is<sup>6</sup>

$$k_b = \frac{(R_2 - R_1)(R_\infty - R_0)R_\infty}{a(t_2 - t_1)(R_\infty - R_2)(R_\infty - R_1)R_0}$$

where  $a$  is initial concentration of base and lactone in moles per liter and  $R_0$ ,  $R_1$ ,  $R_2$  and  $R_\infty$  are measured resistances at times 0,  $t_1$ ,  $t_2$  and  $\infty$ , respectively.  $R_0$  was taken as the resistance of a solution of sodium hydroxide of concentration  $a$ .  $R_\infty$  was determined in two ways. In some cases the conductivity cell for the rate experiment was removed from the bath, kept at room temperature overnight and then brought back to bath temperature and the resistance measured. In other cases solutions identical with those for the rate experiments were made up at room temperature, permitted to react for several hours, put into the conductivity cell, brought to temperature and

(1) Presented in part at the 116th meeting of the American Chemical Society, Atlantic City, N. J., Sept. 19–23, 1949.

(2) Johansson, *Chem. Zentr.*, **87**, 11, 558 (1916).

(3) Olson and Miller, *THIS JOURNAL*, **60**, 2687 (1938).

(4) Olson and Hyde, *ibid.*, **63**, 2359 (1941).

(5) Gresham, Jansen and Shaver, *ibid.*, **70**, 998 (1948).

(6) Hegen and Wolfenden, *J. Chem. Soc.*, 508 (1939).

the resistance measured. The two methods gave results which agreed closely.

For runs at 6.90 and with concentrations of 0.003 molar or lower a slow, unexplained drift in the  $R_{\infty}$  value occurred and, depending on the choice of  $R_{\infty}$ , the calculated values of the rate constants varied as much as ten per cent. For all calculations the value of  $R_{\infty}$  at very long times was somewhat arbitrarily chosen. It may be seen in Table II that somewhat different values of the rate constant are obtained in the 0.005 molar solutions as compared to the values for the 0.003 or 0.002 molar solutions. Because of the difficulty with  $R_{\infty}$  the latter should probably be given less weight.

The neutral, pH independent hydrolysis was studied by both titration and dilatometric procedures. Solutions of lactone were made up using either pure water or salt or buffer solutions. In the titration procedure 10-ml. aliquots of the reacting mixture were removed from time to time, added to 90 ml. of ice water and titrated immediately (to a brom thymol blue end-point) using care so that no part of the solution became basic before the final end-point. Preliminary tests showed that this procedure determined only the acid formed by the hydrolysis and did not cause further hydrolysis of the lactone. Since the hydrolysis of  $\beta$ -propiolactone goes to completion in acid as well as basic solutions, calculation of the reaction rate from the titration data is quite straightforward.

Studies of the acid catalyzed hydrolysis could not be made with any precision by a titration procedure and consequently a dilatometric procedure was used. The volume decrease when the lactone hydrolyzes is comparatively large so that a relatively simple dilatometer was adequate. The ones used consisted of an approximately 50-ml. bulb to which was attached a filling tube that could be closed by a stopcock and a long, open ended capillary tube of about 1 mm. diameter behind which was attached a scale for reading the meniscus height. Usually a small droplet of mercury was placed above the solution meniscus to cut down evaporation. The temperature of the water-bath for the dilatometer was maintained at  $25 \pm 0.004^{\circ}$ . Calculations for the dilatometer runs were generally made using the equation

$$k = \frac{1}{t} \ln \frac{v_0 - v_{\infty}}{v_t - v_{\infty}}$$

where  $t$  is time in minutes and  $v_0$ ,  $v_{\infty}$  and  $v_t$  are volume scale readings at initial time, final time and time  $t$ , respectively. In a few cases calculations were made using the procedure of Guggenheim<sup>7</sup> with closely comparable results.

### I. Hydrolysis in Basic Solution

Tables I and II give data on the rate constants for the bimolecular reaction between the lactone

(7) Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

and hydroxide ion at  $0.07^{\circ}$  and  $6.90^{\circ}$ . Concentrations of lactone and base are equal in all the experiments reported and vary from 0.002 to 0.010 mole per liter. As may be seen in the tables, the temperature varied slightly in the various runs (although it was constant to  $\pm 0.005^{\circ}$  within each run). The observed rate constants were corrected to the standard temperatures of  $0.07^{\circ}$  and  $6.90^{\circ}$  by use of an approximate value of the temperature coefficient.

TABLE I  
SUMMARY OF DATA FOR BASIC HYDROLYSIS OF  $\beta$ -PROPIOLACTONE AT  $0.07^{\circ}$

Temp., °C.	Initial concn. of lactone and base, moles/l.	$k_b$ in l./mole/min.	
		Uncor.	Cor. to $0.07^{\circ}$
0.09	0.010	16.66	16.61
.10	.010	16.63	16.55
.06	.010	17.17	17.20
.06	.010	15.89	15.92
.07	.010	16.71	16.71
.09	.010	16.85	16.80
.06	.010	16.62	16.65
.09	.010	16.11	16.06
.08	.003	16.45	16.42
.08	.003	17.12	17.09
.03	.003	16.55	16.65
.04	.005	16.27	16.35
.01	.005	16.55	16.70
.02	.005	16.90	17.02
Average			16.62

TABLE II  
SUMMARY OF DATA FOR BASIC HYDROLYSIS OF  $\beta$ -PROPIOLACTONE AT  $6.90^{\circ}$

Temp., °C.	Initial concn. of lactone and base, moles/l.	$k_b$ in l./mol./min.	
		Uncor.	Cor. to $6.90^{\circ}$
6.87	0.005	31.0	31.1
6.95	.005	30.7	30.5
6.90	.005	29.7	29.7
Average			30.5
6.86	0.003	29.7	29.9
6.90	.003	31.6	31.6
6.88	.003	29.3	29.4
6.89	.003	30.9	30.9
6.90	.002	29.7	29.7
6.91	.002	28.6	28.6
6.96	.002	29.7	29.4
6.87	.003	30.8	30.9
6.85	.002	29.0	29.2
6.88	.002	28.4	28.5
Average			29.1

A few determinations were made at  $6.90^{\circ}$  with unequal concentrations of lactone and base. Although the rate constants obtained agree roughly with those of Table II, they are not considered as reliable and are consequently not reported.

The measured rate constant in basic solutions is of course a composite one with contributions from both the hydroxide ion and the water re-

actions. However in the solutions studied here the latter reaction in no case makes a contribution as large as 0.5 per cent. so no correction for it has been made.

Figure 1 is a plot of  $\log k_b$  against  $1/T$  for the basic reaction. Johansson's experimental value of  $k_b = 119$  at  $25^\circ$  (measured by a titration procedure) is included although it has been given less weight. From the straight line of Figure 1 the values of the constants  $A$  and  $E$  in the Arrhenius equation,  $k = Ae^{-E/RT}$ , calculate to be  $1.43 \times 10^{10}$  l./mole/sec. and 13.4 kcal. per mole, respectively.

Table III gives a comparison of rates and the Arrhenius constants for the basic hydrolysis of the three lactones,  $\beta$ -propio,  $\beta$ -butyro and  $\gamma$ -butyro. It can be seen that the rate constants at  $25^\circ$  are quite similar for the three lactones although the Arrhenius constants for the  $\beta$ -propio- and  $\gamma$ -butyrolactones are significantly different.

TABLE III

Lactone	$k_b$ , l./mole/min.		Arrhenius constants	
	$0^\circ$	$25^\circ$	$E$ , kcal.	$\log A$
$\beta$ -Propio-	16.6	130 (calcd.)	13.4	10.155
$\beta$ -Butyro- <sup>1</sup>		49		
$\gamma$ -Butyro- <sup>5</sup>	11.8	70 (calcd.)	11.3	8.344

## II. Neutral Hydrolysis (Water Reaction)

The hydrolysis of the  $\beta$ -propiolactone in neutral or slightly acid solutions is accurately first order over at least 90% of the course of reaction. The reaction has been studied at temperatures of 11.68, 25.00 and  $37.28^\circ$  for solutions of lactone in pure water, in buffer solutions and in salt solu-

TABLE IV

WATER REACTION OF  $\beta$ -PROPIOLACTONE AT  $25^\circ$ ; INITIAL LACTONE CONCENTRATION IS APPROXIMATELY 0.08 MOLAR

Method of following	$k_w \times 10^3$ , min. <sup>-1</sup>	Comment
Titration	3.28	Buffered at pH 3.6
Titration	3.37	No buffer, pH shift with reaction
Titration	3.32	No buffer, pH shift with reaction
Titration	3.34	0.0038 M H <sub>2</sub> SO <sub>4</sub>
Dilatometer	3.30	.0038 M H <sub>2</sub> SO <sub>4</sub>
Dilatometer	3.29	.1511 M HClO <sub>4</sub>
Dilatometer	3.26	.1511 M HClO <sub>4</sub>

TABLE V

SUMMARY OF DATA AT  $11.68^\circ$  AND  $37.28^\circ$  FOR NEUTRAL OR SLIGHTLY ACID HYDROLYSIS OF  $\beta$ -PROPIOLACTONE (NO SALT ADDED)

Temp., $^\circ$ C.	Initial lactone concentration, mole/liter	$k_w \times 10^3$ , min. <sup>-1</sup>
11.68	0.1004	0.695
11.68	.0969	0.704
11.68	.113	0.717
37.28	.0519	12.08
37.28	.0716	11.80
37.28	.0967	11.92

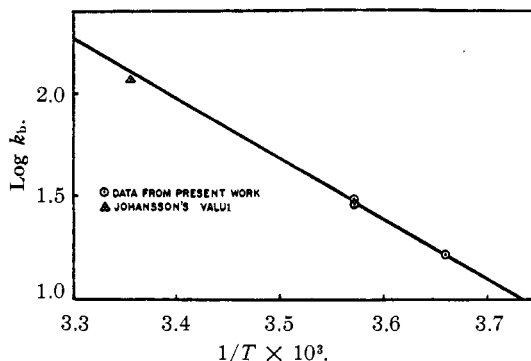


Fig. 1.— $\log k_b$  vs.  $1/T$  for hydrolysis of  $\beta$ -propiolactone in basic solutions.

tions. In all cases the lactone concentration was in the range of from 0.03 to 0.10 mole per liter.

Table IV gives a partial summary of the data for the reaction at  $25^\circ$  and Table V gives data at  $11.68^\circ$  and  $37.28^\circ$ . The data of Table IV show that the dilatometric and titration procedures give similar values for the rate constant and that the rate of the reaction is essentially independent of the acid concentration up to at least 0.15 molar hydrogen ion. The best value of the rate constant in solutions of low ionic strength is  $k_w = 3.32 \times 10^{-3}$  min.<sup>-1</sup>. This compares well with Johansson's<sup>2</sup> value of  $3.5 \times 10^{-3}$  considering that Johansson worked with considerably more concentrated solutions of lactone. At  $11.68^\circ$  the best value of  $k_w$  is  $0.705 \times 10^{-3}$  min.<sup>-1</sup> and at  $37.28^\circ$  the best value is  $11.93 \times 10^{-3}$ .

For the  $\beta$ -butyrolactone Johansson reports a value for  $k_w$  at  $25^\circ$  of about  $8.5 \times 10^{-4}$ , indicating that the water reaction is only about a fourth as fast for the  $\beta$ -butyro- as for the  $\beta$ -propiolactone.

Figure 2 gives a plot of  $\log k_w$  vs.  $1/T$  for the water reaction. It is clear that the data fit the Arrhenius equation very well. The values of the Arrhenius constants are  $E = 19.5$  kcal. and  $A = 1.1 \times 10^{10}$  sec.<sup>-1</sup>. Thus the energy of activation for the water reaction is notably higher than for the reaction with hydroxide ion.

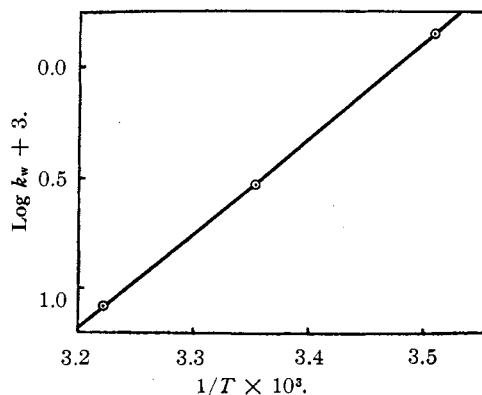


Fig. 2.— $\log k_w$  vs.  $1/T$  for water reaction of  $\beta$ -propiolactone.

A series of runs were made on the water reaction in dilute salt solutions and the data are plotted in Fig. 3. From this figure it is seen that sodium perchlorate and silver or potassium nitrate give at most only a slight salt effect. The large rate increase with chlorides and with sodium acetate indicates an added effect. Actually Gresham, Jansen, Shaver and Gregory<sup>8</sup> have shown that in concentrated solutions both chloride and acetate ions react with  $\beta$ -propiolactone to give  $\beta$ -chloropropionic and  $\beta$ -acetopropionic ions, respectively. Similar reactions of  $\beta$ -lactones have been reported by others.<sup>9,10</sup> Undoubtedly the large apparent rate of hydrolysis in chloride solutions is due to the fact that both a water and a chloride ion reaction are occurring.

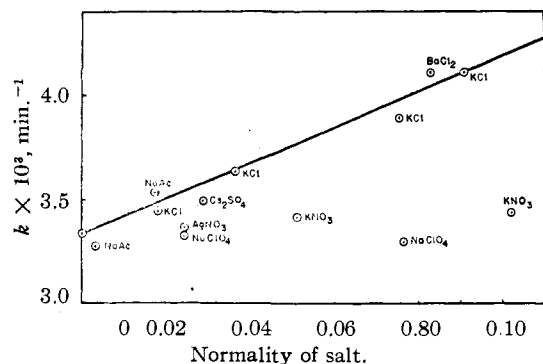
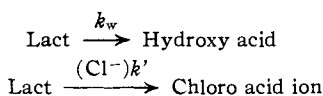


Fig. 3.—Specific reaction rate at 25° for  $\beta$ -propiolactone in neutral solutions containing salt.

The rates given in Fig. 3 were all obtained by titrating acid formed as a function of time and applying the equation  $k_{\text{obs}}t = \ln A_{\infty}/(A_{\infty} - A_t)$  where  $A_{\infty}$  and  $A_t$  are concentration of acid at times  $\infty$  and  $t$ . It is easy to show that for the case of two simultaneous first order reactions



the sum of the rate constants,  $k_w + (\text{Cl}^-)k'$ , is given by  $1/t \ln A_{\infty}/(A_{\infty} - A_t)$  where  $A$  again refers to acid formed. (This assumes that chloride ion concentration is constant which is an approximation but not a bad one.) Thus the data in Fig. 3 may be used to obtain a rough value for  $k'$ , the bimolecular rate constant for the lactone-chloride ion reaction. The value obtained from the solid line of Figure 3 is  $8.5 \times 10^{-3}$  liter/mole/min.

### III. Hydrolysis in Strong Acid Solutions

Preliminary experiments showed that in rather concentrated solutions of strong acids there is an acid catalyzed hydrolysis of the  $\beta$ -propiolactone similar to that found by Olson and Miller<sup>3</sup> for

(8) Gresham, Jansen, Shaver and Gregory, *THIS JOURNAL*, **70**, 999 (1948).

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

(10) Olson and Miller, *THIS JOURNAL*, **60**, 2687 (1938).

$\beta$ -butyrolactone, and we have studied this acid catalysis at 25° over a wide range of acid concentration using three different strong acids. In all cases the acid reaction showed itself to be accurately first order over at least 90% of the reaction.

The measured rate constant is composed of the sum of  $k_w$  for the water reaction and  $k_a = kF$  ( $\text{H}_3\text{O}^+$ ) for the acid reaction where  $F(\text{H}_3\text{O}^+)$  is an undetermined function of hydrogen ion. Values of  $k_a$  are obtained by subtracting  $k_w$  from the observed first order rate constant. Values of  $k_w$  to use to calculate  $k_a$  were obtained from the equation

$$k_w = k_w^0 a_{\text{H}_2\text{O}} = 3.32 \times 10^{-3} a_{\text{H}_2\text{O}}$$

where  $a_{\text{H}_2\text{O}}$  is the activity of water in the given solution and  $k_w^0$  is the value of the rate constant for the water reaction in dilute electrolyte solutions. This equation results from the usual Brönsted-Eyring equation,

$$k_w = k_w^0 (f_{\text{Lact}} a_{\text{H}_2\text{O}} / f_M)$$

if one assumes that the first order water reaction is actually a bimolecular reaction between lactone and water and that  $f_{\text{Lact}}/f_M$ , the ratio of the activity coefficients of the lactone and activated complex, is equal to one. Fortunately in strong acid solutions where this calculated value of  $k_w$  is most uncertain it is only a small fraction of the observed rate constant.

Table VI gives data on the acid catalyzed reaction in aqueous solutions of sulfuric, perchloric and nitric acids. The first column gives acid and concentration; the next column gives the activity of water; the third column gives the calculated values of  $k_w$ . Columns four, five and six give  $k_{\text{obs}}$ ,  $k_a$  and  $\log k_a$ . The values in the last column will be discussed later. For all runs listed the lactone concentration was in the range of from 0.05 to 0.10 molar.

TABLE VI  
HYDROLYSIS AT 25° IN STRONG ACID SOLUTIONS

Acid and concn., M	$a_{\text{H}_2\text{O}}$	$k_w \times 10^3$	$k_{\text{obs}} \times 10^3$	$k_a \times 10^3$	$\log k_a + 3$	$H_0$
HClO <sub>4</sub> 1.834	0.916	3.04	3.65	0.61	-0.215	-0.58
HClO <sub>4</sub> 2.60	.862	2.86	5.38	2.52	.401	-0.94
HClO <sub>4</sub> 2.75	.850	2.82	5.21	2.39	.378	-1.01
HClO <sub>4</sub> 3.26	.804	2.67	8.89	6.22	.794	-1.24
HClO <sub>4</sub> 3.93	.734	2.44	14.41	11.97	1.078	-1.55
HClO <sub>4</sub> 4.53	.665	2.21	32.2	30.1	1.479	-1.84
HClO <sub>4</sub> 4.58	.659	2.19	32.6	30.4	1.483	-1.85
HClO <sub>4</sub> 5.36	.567	1.88	69.9	68.0	1.833	-2.28
NaClO <sub>4</sub> 4.0	(0.5)	1.16	17.6	16.4	1.215	-1.72
HClO <sub>4</sub> 2.0						
H <sub>2</sub> SO <sub>4</sub> 2.01	.903	3.00	5.39	2.39	0.378	-0.73
H <sub>2</sub> SO <sub>4</sub> 3.14	.810	2.69	9.52	6.83	0.834	-1.28
H <sub>2</sub> SO <sub>4</sub> 3.77	.744	2.47	13.1	10.6	1.025	-1.57
H <sub>2</sub> SO <sub>4</sub> 3.92	.728	2.42	18.86	16.44	1.216	-1.64
H <sub>2</sub> SO <sub>4</sub> 5.07	.595	1.98	57.3	55.3	1.743	-2.22
HNO <sub>3</sub> 3.86	.826	2.74	7.46	4.72	0.674	-1.16
HNO <sub>3</sub> 6.73	.66	2.2	29.4	27.2	1.435	-1.87

<sup>a</sup> Water activities from: (a) HClO<sub>4</sub> solutions, Robinson and Baker, *Trans. Proc. Roy. Soc. New Zealand*, **76**, 250 (1946); (b) H<sub>2</sub>SO<sub>4</sub> solutions, Harned and Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 436; (c) HNO<sub>3</sub> solutions, Landolt-Börnstein, Table III, p. 2145.

The most striking point about the data of Table VI is the lack of correlation between rate and concentration of hydrogen ion. For example an increase in perchloric acid concentration of from 2.75 to 5.36 molar causes the value of  $k_a$  to increase by almost 30 fold. Almost as striking is the difference among acids. The rate constant for 3.86 molar nitric acid is less than half of the value for the same molarity of sulfuric or perchloric acid. A final point is the very large salt effect indicated by the high rate in a mixture of 2 molar perchloric acid and 4 molar sodium perchlorate as compared with 2 molar perchloric acid alone.

If instead of the molar concentration of hydrogen ion one considers the acidity of the solutions as measured by  $H_0$ , the Hammett acidity function, the observed variations in the rate are entirely sensible. The values of  $H_0$  in the last column of Table VI are all obtained from the data of Hammett and Paul<sup>11</sup> except that the value for the salt-acid mixture is from data of Dodson and Harbottle.<sup>12</sup> Figure 4 gives a plot of  $\log k_a$  versus  $-H_0$ . The solid line in this figure is drawn with a slope of 1.0, the theoretical slope for first order dependence on the acidity as measured by  $h_0$ , the antilog of  $-H_0$ . It can be seen that the data for all the various solutions fall very close to a line of this slope. It may be concluded that the rate of the acid catalyzed hydrolysis of  $\beta$ -propiolactone is proportional to the acidity of the solutions as measured by  $h_0$  and not at all to the molar concentration of hydrogen ion.

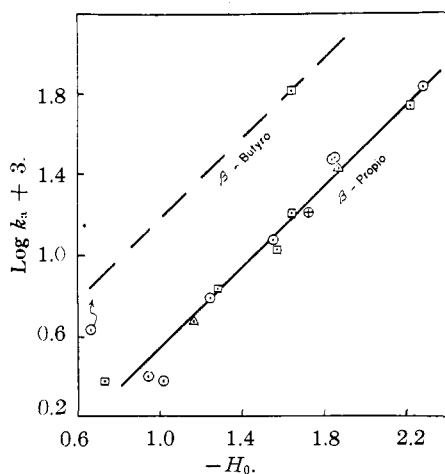


Fig. 4.— $\log k_a$  vs.  $-H_0$  for acid-catalyzed hydrolysis of  $\beta$ -propiolactone at 25°. Dotted line is Olson and Miller data for  $\beta$ -butyrolactone solutions:  $\circ$ ,  $\text{HClO}_4$ ;  $\square$ ,  $\text{H}_2\text{SO}_4$ ;  $\Delta$ ,  $\text{HNO}_3$ ;  $\oplus$ ,  $\text{HClO}_4$  and  $\text{NaClO}_4$ .

For the  $\beta$ -butyrolactone at 25° Olson and Miller give for the water reaction  $k_w = 8.5 \times 10^{-4}$  min.<sup>-1</sup>. In 2 molar perchloric acid  $k_{\text{obs}}$  was  $12 \times 10^{-4}$  and in 3.94 molar sulfuric acid  $k_{\text{obs}}$  was

$72 \times 10^{-4}$ . Olson and Miller plotted their observed rate constants against  $p\text{H}$  and could only reconcile the sulfuric acid data by quite arbitrarily assigning an activity of 7.87 to the hydrogen ion in their 3.94 molar sulfuric acid solution. Although two values of rate constants are not really sufficient for a definite conclusion it is of interest that these data, after correction for  $k_w$  in the same manner as before, fall fairly well on an  $H_0$  plot with slope 1. This may be seen in Figure 4 which includes the two points of Olson and Miller. At a given value of  $H_0$  the acid reaction for the  $\beta$ -butyrolactone is about 4 times as fast as that for the  $\beta$ -propiolactone.

#### IV. Discussion

The data given for the  $\beta$ -propiolactone indicate that its hydrolysis in acid, basic and neutral solutions is very similar to the hydrolysis of the  $\beta$ -butyrolactone. This is illustrated by Fig. 5 which is a plot of the logarithm of the rates for the two lactones against  $H_0$  (which is identical with  $p\text{H}$  in solutions of low acidity). Incidentally it may be noted in Fig. 5 that substitution of a methyl group on the  $\beta$ -carbon of the  $\beta$ -propiolactone causes changes in rates in just the directions predicted by the greater electron release character of a methyl group relative to a hydrogen. The methyl group results in a decrease in rate for the reaction of hydroxide ion on the carboxyl carbon, a relatively larger decrease in rate for the reaction of water on the  $\beta$ -carbon and, finally, an increase in rate for the reaction of the positively charged hydrogen ion. There can be little doubt that the mechanisms of hydrolysis are identical for the two lactones, *i. e.*, that the alkyl-oxygen fission found by Olson and Hyde for the water reaction with the  $\beta$ -butyrolactone occurs also with the  $\beta$ -propio compound and that acyl-oxygen fission occurs for the basic and acid catalyzed reactions.

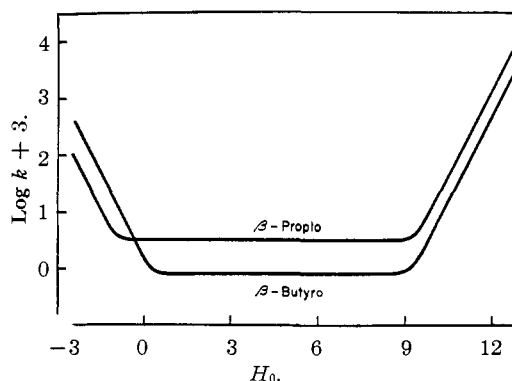


Fig. 5.— $\log k$  vs.  $H_0$  for two  $\beta$ -lactones at 25°:  $k = k_w + k_1 h_0 + k_2 \text{COH}^-$ .

A related point of some interest is the bearing of the hydrolysis results on the alcoholysis reactions of  $\beta$ -propiolactone reported by Gresham,

(11) Hammett and Paul, *THIS JOURNAL*, **56**, 827 (1934).

(12) Private communication.

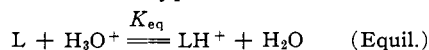
*et al.*<sup>13</sup> These investigators studied the alcoholysis reactions in concentrated solutions of lactone in alcohols and determined relative amounts of products. They report that the base catalyzed reaction gives primarily esters of hydracrylic acid, the expected product for acyl-oxygen fission. With neutral or slightly acid solutions the chief products are alkoxy derivatives indicating alkyl-oxygen fission. (In all cases approximately 20% of polymeric products are formed.) In solutions containing increasingly larger amounts of sulfuric acid the amount of alkoxy derivatives decreases and the amount of hydracrylic acid derivatives increases. This is strongly suggestive of the entrance of an acid catalyzed reaction involving acyl-oxygen fission. Gresham, *et al.*, explain the increased production of hydracrylate derivatives in the more acid solutions by a polymerization followed by a depolymerization reaction involving further alcohol. However, the direct entrance of an acid catalyzed reaction involving acyl-oxygen fission seems quite likely and is consistent with the results in aqueous solutions.

The point of greatest interest with the  $\beta$ -propiolactone hydrolysis is the correlation of the rate of the acid reaction with  $H_0$ . This acidity function is defined by Hammett as

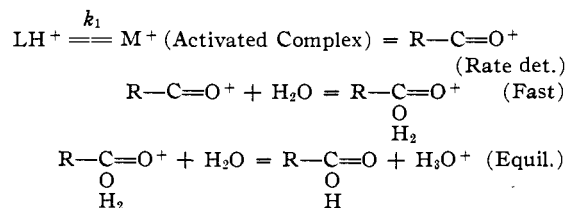
$$H_0 = -\log(a_{H^+}f_B/f_{BH^+})$$

where  $a_{H^+}$  is activity of hydrogen ion and  $f_B$  and  $f_{BH^+}$  are activity coefficients of a neutral base and its conjugate acid. The question is, what is indicated about the mechanism of the lactone hydrolysis by the observed dependence on  $H_0$ ? Day and Ingold<sup>14</sup> point out in their excellent discussion of the mechanisms of ester hydrolysis that there is evidence for two mechanisms for the acid catalyzed reaction, both involving fission of the acyl-oxygen bond. These are given below, modified for the particular case of lactone hydrolysis.

Both mechanisms involve a preliminary acid-base equilibrium of the type



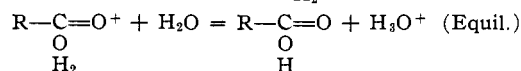
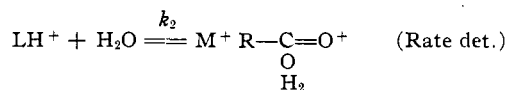
For the A'-1 mechanism this is followed by a rate determining unimolecular rearrangement to give an acylium ion. The water molecule then adds in a follow reaction.



The A'-2 mechanism differs in that the water molecule is involved in the rate determining step

(13) Gresham, Jansen, Shaver, Gregory and Beears, *THIS JOURNAL*, **70**, 1004 (1948).

(14) Day and Ingold, *J. Chem. Soc.*



In all of the above equations the group R includes a hydroxyl group.

For the A'-1 mechanism the predicted rate equation is

$$\text{Rate} = k_1 K_{eq} C_L \frac{C_{H_3O^+} f_{H_3O^+} f_L}{a_{H_2O} f_{M^+}} = k_1 C_L \frac{a_{H^+} f_L}{f_{M^+}} = k_a C_L$$

Since in the A'-1 case the lactone and the activated complex differ only by a proton it is plausible that the ratio  $f_L/f_{M^+}$  will vary with medium changes in the same way as does the activity coefficient ratio  $f_B/f_{BH^+}$  for a base and its conjugate acid and this will lead to proportionality of  $\log k_a$  to  $H_0$ .<sup>15</sup>

The rate expression for the A'-2 mechanism is

$$\text{Rate} = k_2 K_{eq} C_L C_{H_3O^+} (f_L f_{H_3O^+} / f_{M^+}) = k_a' C_L$$

In this case the lactone and activated complex differ by both a proton and a water molecule and it is much less likely that  $f_L/f_{M^+}$  and  $f_B/f_{BH^+}$  will vary in the same way as the medium changes. In fact, if the ratio  $f_L f_{H_3O^+} / f_{M^+}$  is approximately constant the rate will vary with the molar concentration of hydronium ion rather than with  $h_0$ . The situation here is similar to the iodination of acetophenone<sup>16</sup> where a formally rather similar mechanism prevails and where the rate is proportional to concentration of acid and not to  $h_0$ .

Day and Ingold point out that mechanism A'-2 is the usual mechanism for hydrolysis of aliphatic esters and that mechanism A'-1 will normally tend to occur only in highly ionizing solvents. Data on the acid catalyzed hydrolysis of  $\gamma$ -butyrolactone<sup>17</sup> indicate that this hydrolysis (and presumably therefore that of ordinary esters) is proportional to molar concentration of strong acid and not to  $H_0$ . Although Hammett and Paul<sup>18</sup> state that the acid hydrolysis of ethyl acetate appears to be proportional to  $H_0$  not much weight can be given to this since, as was pointed out by Zucker and Hammett,<sup>16</sup> the data do not go to high enough acid concentration for the distinctive character of  $H_0$  to appear.

On the basis of the dependence of the rate on  $H_0$  it appears that the acid catalyzed hydrolysis of  $\beta$ -lactones goes through an acylium ion or A'-1 type of mechanism and thus differs from ordinary ester hydrolysis. The explanation of this is doubtless connected with the large ring strain characteristic of  $\beta$ -lactones. This ring strain presumably permits the unimolecular rupture of the acyl C-O bond of the  $\beta$ -lactone whereas with the  $\gamma$ -lactone a simultaneous

(15) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 275.

(16) Zucker and Hammett, *THIS JOURNAL*, **61**, 2791 (1939).

(17) F. A. Long and Frances Dunkle, unpublished data, this laboratory.

(18) Hammett and Paul, *ibid.*, **56**, 830 (1934).

formation of a new bond to a water molecule is required.

### Summary

1. Data on the rate of reaction in aqueous solutions between  $\beta$ -propiolactone and hydroxide ion at 0.07° and 6.90° are presented.

2. Data are given on the rate of reaction between water and  $\beta$ -propiolactone at 11.68, 25.00 and 37.28°. Between pH values of 0 and 7 this water reaction is the only one which occurs. A preliminary study of salt effects on this reaction has been made. Sodium perchlorate and silver or potassium nitrate at concentrations up to 0.1 molar cause little or no change in rate. A large apparent effect of sodium chloride is due to en-

trance of a reaction of the lactone with chloride ions.

3. An acid catalyzed hydrolysis of the lactone occurs in aqueous solutions of strong acids when the acid concentration is 2 molar or higher. This reaction has been studied at 25° in solutions of perchloric, sulfuric and nitric acids. The rate of hydrolysis is accurately proportional to  $H_0$ , the Hammett acidity function, and not at all to molar concentration of strong acid. The result suggests that the mechanism of the acid catalyzed hydrolysis of the  $\beta$ -lactone differs from that of  $\gamma$ -lactones and most aliphatic esters and that the reaction goes through the A'-1 mechanism of Day and Ingold.

ITHACA, NEW YORK

RECEIVED JANUARY 3, 1950

## NOTES

### A Thermal Reaction in Neutron-Irradiated Permanganates

BY A. H. W. ATEN, JR. AND J. B. M. VAN BERKUM

An entirely new possibility for the study of chemical processes in crystal lattices has been demonstrated in a recent paper by Green and Maddock.<sup>1</sup> These authors activated potassium chromate with slow neutrons and determined the retention in the irradiated product both after subsequent heating and without. It is evident that this method furnishes data about thermal reactions between two types of atoms within a crystal lattice, the over-all structure of which is left intact during the process.

We have been interested in the same kind of reactions, and we considered that potassium permanganate, which is known to suffer thermal decomposition around 200°, should offer a fair chance for the observation of this type of process. Our results, listed in Table I, show that the thermal reaction is quite slow below about 90°.

TABLE I

THERMAL REACTION OF RADIOACTIVE MANGANESE IN NEUTRON-IRRADIATED POTASSIUM PERMANGANATE

Temp., °C.	Fraction of total activity in reduced state		
	Unheated (0.70)	Heated 20 min.	Heated 120 min.
From Libby's graph			
85	.79	..	0.64
	.78	..	.65
180	..	0.33	0.26
	.77	.30	.27
	.74	.35	.30

(1) J. H. Green and A. G. Maddock, *Nature*, **164**, 788 (1949).

Just as in the experiment of Green and Maddock the entire activity does not return to the original ion and more prolonged heating does not make much difference in this respect. It is evident that not all radioactive atoms are subject to the same reaction. It is worth noticing that in the case of potassium permanganate the fraction of the total activity associated with the reduced valency does not decrease below one-fourth of the total activity on heating, whereas it is reduced to about 5% in potassium chromate.

A thin layer of small crystals of potassium permanganate was exposed to slow neutrons from 100 mc. radium-beryllium. (If the material is ground to a fine powder before heating, the thermal reaction does not go as far as it does with whole crystals during the same time.) In most experiments two or three samples of the same irradiated batch were treated simultaneously. Some were heated to the required temperature as rapidly as possible and one was kept at room temperature and used as a blank. All were dissolved in 0.02 *N* sulfuric acid and mixed with a small quantity of dissolved manganese sulfate. The manganese dioxide was filtered through a small paper filter without suction. After this the permanganate solution was reduced and precipitated as the dioxide. A rough estimate of the accuracy of the separation may be obtained from the differences between the figures in the last column of Table I and from a comparison with experiments by Libby.<sup>2</sup> The distribution of radioactivity in unheated samples was also determined in ten other cases. The figures obtained ranged between 0.75 and 0.82, indicating a very satisfactory reproducibility.

It should be mentioned that in our preparation decomposition began just about 180°. A slight change of color could sometimes be detected in the surface, but the loss of weight was negligible.

INSTITUTE FOR NUCLEAR RESEARCH  
AMSTERDAM, NETHERLANDS

RECEIVED NOVEMBER 19, 1949

(2) W. F. Libby, *This Journal*, **62**, 1930 (1940).