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SCHOOL OF FORESTRY
DIVISION OF AGRICULTURAL BIOCHEMISTRY
UNIVERSITY OF MINNESOTA
ST. PAUL, MINNESOTA

Arrhenius Parameters for Acid Hydrolysis of γ -Butyrolactone; Search for a Reaction with Water

BY FRANCES DUNKLE COFFIN¹ AND F. A. LONG

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Detailed kinetic and equilibrium studies of the acid-catalyzed hydrolysis of γ -butyrolactone have been reported at only one temperature, 25°. In connection with a broader study of this reaction² we have investigated rates and equilibria in dilute acid solutions at three temperatures, and from these data have calculated the heat of reaction and energies of activation. A search for an uncatalyzed hydrolysis of this lactone was also made. Evidence for such a reaction of the γ -lactones is inconclusive²⁻⁴ although it occurs readily with β -lactones.⁵ The rates and equilibrium were determined by titration of the hydroxy acid formed. Hydrochloric acid was the only catalyst used since earlier studies² showed the rate to be independent of the particular strong acid employed. Temperatures were constant to $\pm 0.005^\circ$.

Since the hydrolysis reaction is reversible, the first-order rate constant for the forward reaction is given by

$$k'_h = \frac{1}{(1+K)t} \ln \frac{1}{1 - (1+K)C_{HA}/C_{L_0}}$$

where C_{L_0} is initial lactone concentration, C_{HA} is concentration of hydroxy acid formed and K is the concentration equilibrium constant, *i.e.*, $K = k'_1/k'_h = C_{L(eq)}/C_{HA(eq)}$. From the values of K and k'_h , the rate constant, k'_1 , for the reverse reaction may be determined; the second-order rate constants k_h and k_1 for the forward and reverse reactions with hydrogen ion may be calculated from the relations $k'_h = k_h/C_{H^+}$ and $k'_1 = k_1/C_{H^+}$.

Table I gives detailed data on k'_h , k_h and K at 39°, and the average values of K and k_h at 25 and 50°. The agreement between the present results at 25° and those of earlier workers² is excellent. From the equilibrium constants of Table I, ΔH for the hydrolysis reaction is calculated to be -710 calories.

The observed constancy of k_h at each temperature indicates that the reaction is accurately first-order in the concentration of hydrogen ion. On the basis of studies with added electrolytes,³ a salt effect might be expected for both rates and equilibria, but the electrolyte concentrations are so

(1) Holder of a Wilson College Fellowship, Sept., 1945, to June, 1948.

(2) (a) P. Henry, *Z. physik. Chem.*, **10**, 96 (1892); (b) H. Johansson and H. Sebelius, *Ber.*, **51**, 480 (1918); (c) A. Kailan, *Z. physik. Chem.*, **94**, 111 (1920); **101**, 63 (1922).

(3) (a) F. A. Long, W. F. McDevit and Frances B. Dunkle, *J. Phys. Colloid Chem.*, **55**, 813 (1951); (b) F. A. Long, Frances B. Dunkle and W. F. McDevit, *ibid.*, **55**, 829 (1951).

(4) E. J. Boorman and R. P. Linstead, *J. Chem. Soc.*, 577 (1933).

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TABLE I

t , °C.	ACID HYDROLYSIS OF γ -BUTYROLACTONE				
	C_{L_0} , mole/l.	C_{H^+} , mole/l.	K	$10^4 k'_h$, min. ⁻¹	$10^4 k_h$, 1. mole ⁻¹ min. ⁻¹
39.00	0.1023	0.01008	2.74	4.90	4.86
	.1025	.01008	2.78	4.88	4.84
	.0934	.0427	2.72	19.29	4.79
	.0835	.04025	2.87	18.15	4.51
	.3148	.06037	2.77	29.52	4.89
	.3618	.06040	2.79	28.87	4.78
	.0982	.08083	2.87	36.86	4.56
	.0999	.09090	2.88	40.81	4.49
			Av. 2.80	Av.	4.72×10^{-2}
	25.00		Av. 2.67	Av.	1.32×10^{-2}
50.00		Av. 2.93	Av.	11.9×10^{-2}	

low in the present experiments that the effect is negligibly small.

Plots of $\log k_h$ and $\log k_1$ against $1/T$ give excellent straight lines showing that the Arrhenius equation is obeyed. Table II gives the resulting values of energies of activation and frequency factors as well as comparison values for other esters and lactones. The several values of energy of activation are nearly identical but the frequency factors vary considerably.

TABLE II

ARRHENIUS CONSTANTS FOR REACTIONS WITH HYDROGEN ION FOR k IN L. MOLE⁻¹ SEC.⁻¹

Compound	E , cal.	$\log_{10} A$
γ -Butyrolactone		
Hydrolysis	16810	8.67
Lactone formation	17540	9.68
γ -Valerolactone		
Hydrolysis ⁶	16690	7.85
Lactone formation ⁷	16630	9.66
Methyl acetate ⁷	16920	8.59
Ethyl acetate ⁷	16830	8.22

The Water Reaction.—If one makes the assumption that a spontaneous water reaction contributes to the lactone hydrolysis, then the total rate of hydrolysis in dilute aqueous solution would be given by

$$dC_{HA}/dt = [k_w + k_h C_{H^+} + k_b C_{OH^-}] C_L - k_1 C_{HA} C_{H^+} - k'_w C_{HA}$$

From the previous rate data at 50° for the acid hydrolysis and from rate data on the hydroxide ion reaction obtained by extrapolating the results of Hegan and Wolfenden⁸ to this same temperature (which gives $k_b = 296$ at 50°), the optimum pH for detection of the water reaction may be calculated by minimizing the above equation with respect to C_{H^+} . The pH value so determined (for 1% hydrolysis) is 4.9 at 50°.

Several experiments were made on the initial rate of hydrolysis of the lactone at 50° and at pH values close to 5 using acetic acid-sodium acetate buffers. To calculate k_w , a differential form of the above equation was used

(6) H. S. Taylor and H. W. Close, *J. Phys. Chem.*, **29**, 1085 (1925).

(7) E. A. Moelwyn-Hughes, "The Kinetics of Reactions in Solutions," 2nd ed., Clarendon Press, Oxford, 1947, p. 321.

(8) D. S. Hegan and J. H. Wolfenden, *J. Chem. Soc.*, 508 (1958).

$$k_w = (\Delta C_{HA} / \Delta t) - [k_b C_{H^+} + k_b C_{OH^-}] + \frac{[(k_b + k_1) C_{H^+} + k_b C_{OH^-}](C_{HA} / C_{L_0})}{(k_b + k_1) C_{H^+} + k_b C_{OH^-}} \\ \equiv (\Delta R / \Delta t) - Q + PR$$

where R is C_{HA} / C_{L_0} and Q and P are the two bracketed expressions above. ΔR is the change in R for a time change Δt . The term $(k_w + k_w)R$ has been omitted from the above equation since only initial hydrolysis rates were measured. Actually the term PR is also almost negligible. Since all experiments gave very similar results, the data for only one are given in Table III. Values of the ionization constants of acetic acid and water at 50° were obtained from the work of Harned and Ehlers⁹ and Walpole,¹⁰ respectively.

TABLE III
SEARCH FOR WATER HYDROLYSIS AT 50°

Initial conditions:
 $C_{L_0} = 0.1438 M$; $C_{HOAC} = 0.0133 M$; $C_{NAOAC} = 0.032 M$
 $C_{H^+} = 7.2 \times 10^{-6} M$; $C_{OH^-} = 7.7 \times 10^{-9} M$
 $Q = k_b C_{H^+} + k_b C_{OH^-} = 3.1 \times 10^{-6} \text{ min.}^{-1}$
 $P = (k_b + k_1) C_{H^+} + k_b C_{OH^-} = 5.6 \times 10^{-6} \text{ min.}^{-1}$

Rate data:	$\Delta t, \text{min.}$	$10^4 \Delta R / \Delta t, \text{min.}^{-1}$	$10^4 Q, \text{min.}^{-1}$	$10^4 (Q - PR), \text{min.}^{-1}$	$10^4 k_w, \text{min.}^{-1}$
	1435	4.2	0.61	3.1	1.1
	1177	4.5	1.13	3.1	1.4
	3174	4.3	2.48	3.0	1.3
	1465	3.8	3.03	3.0	0.8

The value of the hydrolysis rate to be expected from the known acid-catalyzed and basic reactions, $Q - PR$, is subject to a fairly large error both from the long extrapolation required to obtain k_b at 50° and from errors in measuring the initial hydrolysis rate. Hence there would be convincing evidence for a water reaction only if the calculated k_w were large compared to $(Q - PR)$. Actually the calculated k_w value is only about a third of $(Q - PR)$ and it may be concluded that no good evidence exists for a direct reaction of this lactone with water.

- (9) H. S. Harned and R. W. Ehlers, *This Journal*, **55**, 652 (1933).
 (10) G. S. Walpole, *J. Chem. Soc.*, **105**, 2501 (1914).

DEPARTMENT OF CHEMISTRY
 CORNELL UNIVERSITY
 ITHACA, N. Y.

The Study of Chloroiodides of Silicon, Tin and Germanium Using the Raman Spectra as Proof of Equilibria

By MARIE LOUISE DELWALLE, MARIE BERTHE BUISSET
 AND MICHEL DELHAVE

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The chloroiodides of silicon, tin and germanium have a tetrahedral structure and show the following types of Raman spectra: AX_4 four frequencies and one polarized; AX_3Y six frequencies and three polarized; AX_2Y_2 nine frequencies and four polarized.

Earlier work with the chlorobromides of carbon,¹ silicon,² titanium,³ germanium⁴ and tin⁵ led to the present study of the Raman spectra for chloro-

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 (3) M.-L. Delwalle and F. Francois, *ibid.*, **220**, 173 (1945).
 (4) M.-L. Delwalle and F. Francois, *ibid.*, **227**, 1229 (1948).
 (5) M.-L. Delwalle and F. Francois, *ibid.*, **219**, 64 (1944).

iodides. In the case of the chlorobromides of carbon and silicon three chlorobromides can be isolated whereas for titanium, germanium and tin similar compounds cannot be isolated.

The manner in which the Raman spectra vary was studied^{1,2} for the two series: CCl_4 , CCl_3Br , CCl_2Br_2 , $CClBr_3$, CBr_4 and $SiCl_4$, . . . , $SiBr_4$ (Tables I and II). The two spectral patterns have exactly the same shape. Frequency ν_1 , which is the strongest and the most completely polarized, is of

TABLE I

Frequencies, cm.^{-1}

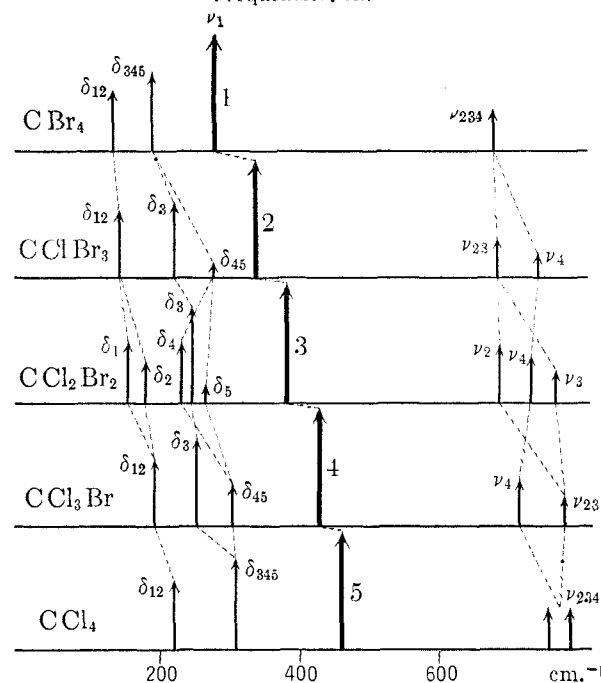


TABLE II

Frequencies, cm.^{-1}

