## Experimental

Dipole moments of I, II, VIII, and IX were measured in dioxane at 30° and calculations made using the equation and method of Halverstadt and Kumler.[16]

We wish to thank Dr. H. K. Hall, Jr., of DuPont for providing glutaric anhydride and cyclohexane 1,3 anhydride.[17]

Phthalimide was from Eastman and naphthalimide was through the courtesy of C. W. French, Jr., of Pfister Chemical Works, Ridgefield, N. J. The latter compounds were recrystallized from dioxane. All spectrographic measurements were made by Mr. M. K. Hrenoff of the Spectrographic Laboratory of the School of Pharmacy. Infrared spectra were run on Perkin-Elmer Model 21 and ultraviolet spectra on Cary Model 11.

**Acknowledgment.**—This paper has been aided by U. S. Public Health Service Grant CY-3211 (C4).

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[16] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

[17] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **80**, 6412 (1958).

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# Acid Hydrolysis of *N*-Butyryl-γ-butyrolactam

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The hydrolysis of *N*-butyryl-γ-butyrolactam in aqueous solution is a pseudo-first-order reaction catalyzed by general acids. The hydronium ion–catalyzed reaction produces butyric acid and γ-butyrolactam. At very low acid concentrations the rate appears to be nonlinear in acid. The reaction exhibits a deuterium solvent isotope effect; $k_H/k_D = 0.83 \pm 0.03$ and it was found that $\Delta H^\ddagger = 18.2 \pm 0.9$ kcal./mole and $\Delta S^\ddagger = -16 \pm 2.5$ e.u. The mechanism of the reaction is discussed and an explanation is offered for the unusual dependence of the rate on acid concentration.

The hydrolysis of carboxylic acid derivatives has long been a favorite field for quantitative investigation and the theory underlying organic chemistry has benefited from these studies. The mechanisms for many of these reactions have been systematized to a certain extent.[1,2] Although the hydrolysis of imides and *N*-acyllactams with basic reagents has been studied,[3,4] the hydrolysis of these materials under acidic conditions has not been investigated in detail.[5–8]

The work herein reported was undertaken in an effort to obtain quantitative information relating to the acid-catalyzed hydrolysis of *N*-butyryl-γ-butyrolactam (I). The rate of hydrolysis was studied in relatively dilute aqueous solution by following the rate of formation of carboxylic acid.

## Experimental

*N*-Butyryl-γ-butyrolactam was prepared by the method of Reppe from γ-butyrolactam and butyric anhydride.[9] The product had b.p. 136°/19 mm. and $n^{25}_{D}$ 1.4760.

*Anal.* Calcd. for $C_8H_{13}NO_2$: C, 61.9; H, 8.44; N, 9.03. Found: C, 61.3; H, 8.5; N, 8.99.

The infrared spectrum of the pure liquid showed no NH or OH absorption and no acidic material was detected by titration.

The hydrolysis of I was carried out in sealed glass ampoules immersed in a silicon oil thermostat of conventional design. The temperature was controlled to ±0.1°. The reaction was followed by periodically removing an ampoule from the oil bath, quenching in cold water, and titrating a pipetted portion (usually 2.0 ml.) of the ampoule's contents conductometrically with standard sodium hydroxide after dilution to an appropriate volume. The total acid concentration in the sample was determined graphically using standard methods.[10] The amount of carboxylic acid produced was then assessed by subtracting the catalyzing acid's concentration where applicable. The results obtained in this way agreed well with carboxylic acid concentrations obtained directly from the conductance curves.

Reaction mixtures used to fill the ampoules were prepared in volumetric flasks from pipetted amounts of stock solutions of the various reagents. It was found that aqueous stock solutions of the substrate underwent slow decomposition at room temperature. Consequently, fresh stock solutions were prepared frequently. This was always done for runs in which the "spontaneous" reaction and acetic acid catalysis were studied. A stock solution of the substrate in deuterium oxide was used for runs in which the solvent isotope effect was investigated.

All of the water employed in preparing the stock solutions, reaction mixtures, and that used in the conductometric titrations was distilled and deionized and had a specific resistance greater than $2 \times 10^6$ ohm-cm. The salts employed were Mallinckrodt Analytical Reagent grade. The hydrochloric and acetic acids were DuPont reagents. The deuterium oxide was a product of the Stuart Oxygen Co. containing greater than 99 atom per cent deuterium. Commercial dioxane was purified using the method outlined by Wyness.[11]

The course of the reaction was determined by hydrolyzing 0.233 mole of *N*-butyryl-γ-butyrolactam with 0.002 mole of *p*-toluenesulfonic acid (0.008 *M*) in aqueous solution by refluxing for several days. The reaction mixture was then exhaustively steam distilled until aliquots of the fresh distillate were free of acid. Titration indicated that 0.228 mole of carboxylic acid was present in the distillate and 0.004 mole of carboxylic acid in addition to the expected *p*-toluenesul-

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[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chap. XIV.

[2] M. L. Bender, *Chem. Rev.*, **60**, 53 (1960).

[3] H. K. Hall, Jr. *et al.*, *J. Am. Chem. Soc.*, **80**, 6420 (1958).

[4] B. M. Regan and F. N. Hayes, *ibid.*, **78**, 639 (1956).

[5] W. H. Mills and J. B. Whitworth, *J. Chem. Soc.*, 2738 (1927).

[6] W. Hückel and F. Stefp, *Ann.*, **453**, 163 (1927).

[7] E. Bamberger and S. Williamson, *Ber.*, **27**, 1458 (1894).

[8] W. Hentschel, *ibid.*, **23**, 2394 (1890).

[9] J. W. Reppe, *Ann.*, **596**, 1 (1955).

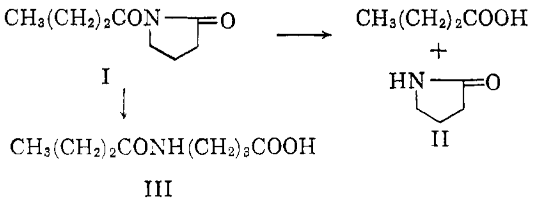
[10] F. Daniels *et al.*, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1949, p. 169.

[11] K. G. Wyness, *J. Chem. Soc.*, 2934 (1958).

fonic acid was present in the residue.[12] Thus, the total yield of carboxylic acid was 0.232 mole (> 99%) and of this at least 98% was butyric acid since the ring cleavage product, *N*-butyryl-γ-aminobutyric acid, does not steam distill.

## Results

**Course of the Reaction.**—A number of the hydrolyses were followed for 8–10 half-lives and the reaction of one equivalent of I led to the formation of one equivalent of acid ±5%.[13] It is possible that the hydrolysis can proceed in two ways to produce either butyric acid and γ-butyrolactam (II) or *N*-butyryl-γ-aminobutyric acid (III):



Isolation of the acidic reaction product indicated that butyric acid is formed almost exclusively in acidic hydrolysis.[14]

**Rate Law.**—The hydrolysis of I was found to be a pseudo first-order reaction and equation 1 was obeyed to well beyond 80% reaction. A typical first-order rate plot illustrating the precision of the data is shown in Fig. 1. The reported rate constants

$$k_1 = -2.303/t \log \text{(fraction unreacted)} \qquad (1)$$

were obtained by drawing the best straight line through the points.

**Substrate Dependence.**—The rate as a function of initial *N*-butyryl-γ-butyrolactam concentration was studied at 93° using 0.00956 *M* hydrochloric acid with the results shown in Table I.

TABLE I

DEPENDENCE OF THE RATE ON *N*-BUTYRYL-γ-BUTYROLACTAM CONCENTRATION

| Substrate, *M* | $k_1 \times 10^4$ Sec.$^{-1}$ |
|---|---|
| 0.00403 | 1.78 |
| .00806 | 1.96 |
| .0210 | 2.27[a] |
| .0609 | 2.24 |
| .1013 | 2.34 |

[a] Average of two runs with an average deviation from the mean, A.D.M., ±0.09 × $10^{-4}$ sec.$^{-1}$.

**Acid Dependence.**—The rate as a function of hydrochloric acid concentration was also determined at 93° using a 0.0210 *M* substrate concentration. The reactions were conducted at constant ionic strength ($\mu$ = 0.02) maintained with sodium chloride. The results are given in Table II.

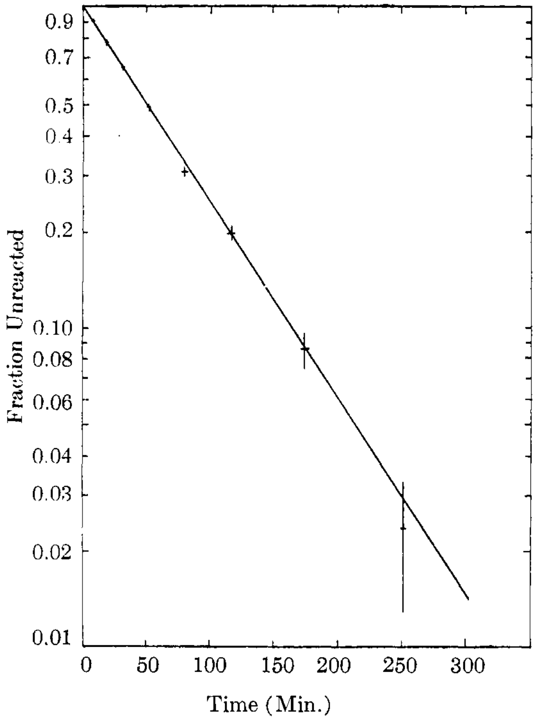


Fig. 1.—First-order rate plot for the hydrolysis of 0.021 *M* *N*-butyryl-γ-butyrolactam with 0.00956 *M* hydrochloric acid at 93.1°.

TABLE II

DEPENDENCE OF THE RATE ON HYDROCHLORIC ACID CONCENTRATION

| HCl, *M* | $k_1 \times 10^4$ Sec.$^{-1}$ | $k_{H^+} \times 10^2 M^{-1}$ Sec.$^{-1a}$ |
|---|---|---|
| 0.00 | 0.058[b] | |
| .000956 | .594 | 5.61 |
| .00478 | 1.53 | 3.08 |
| .00956 | 2.29[c] | 2.33 |
| .0143 | 2.63 | 1.79 |
| .0191 | 3.21 | 1.65[d] |

[a] This is the hydronium ion catalytic constant defined by $k_{H^+} = (k_1 - k_0)/\text{HCl}$. [b] Average of two runs with A.D.M. = ±0.005 × $10^{-4}$ sec.$^{-1}$ defined as $k_0$. The rate constant was determined from data covering the first 10% reaction. At higher extents of reaction curvature in the first order rate plots was observed indicating catalysis by the acidic product. The addition of 0.02 *M* γ-butyrolactam did not change the rate. [c] Average of three runs with A.D.M. = ±0.07 × $10^{-4}$ sec.$^{-1}$. [d] This value for $k_{H^+}$ was used in obtaining the Brönsted correlation presented in the Discussion.

The fact that a "spontaneous" reaction with water was observed led to additional experiments in an effort to ascertain whether molecular acetic acid would also catalyze the hydrolysis. Acetic acid–sodium acetate buffers were employed at constant buffer ratios. Two sets of experiments at different buffer ratios were performed. The ionic strength was maintained constant at $\mu$ = 0.02 with potassium bromide. The substrate concentration was

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(12) Separate experiments have shown that γ-aminobutyric acid would not have been detected in these titrations. However, additional titrations on both distillate and residue employing prior reaction with formaldehyde giving a titratable adduct of γ-aminobutyric acid showed that the reaction produced little, if any, γ-aminobutyric acid.

(13) Unpublished work conducted in these laboratories has shown that the hydrolyses of II and III are about one hundred times slower than the hydrolysis of I under the same experimental conditions.

(14) In contrast, upon conducting the hydrolysis with sodium hydroxide, the infrared spectrum of the product indicated that about two thirds of the product was III.

0.02 $M$ and the temperature 93°. The results constitute Table III.

Table III

Dependence of the Rate on Acetic Acid Concentration

| HOAc/NaOAc | HOAc, $M$ | $k_1 \times 10^6$ Sec.$^{-1}$ | Slope M.$^{-1}$ Sec.$^{-1}$[a] |
|---|---|---|---|
| 1.01 | 0.00201 | 7.63 | |
| | .0101 | 8.44 | |
| | .0201 | 8.62 | $7.6 \times 10^{-5}$ |
| 5.03 | .0101 | 12.7 | |
| | .0503 | 16.0 | |
| | .101 | 18.7 | $7.5 \times 10^{-5}$ |

[a] This is the slope of the line obtained by plotting $k_1$ *vs.* HOAc and is defined as the acetic acid catalytic constant.

**Kinetic Salt Effects.**—The effect of added sodium chloride on the rate of hydrolysis was studied briefly for both the "spontaneous" reaction and the reaction catalyzed by hydrochloric acid. A substrate concentration of 0.02 $M$ was used at 93°. Table IV presents the results obtained.

Table IV

The Influence of Ionic Strength on the Rate

| HCl, $M$ | $\mu$ | $k_1 \times 10^4$ Sec.$^{-1}$ |
|---|---|---|
| 0.00956 | 0.00956 | 2.27 |
| | .0196 | 2.29 |
| | .110 | 2.36 |
| .00 | .00 | 0.032 |
| | .0200 | .058 |

**Solvent Effects.**—The rate of hydrolysis was determined in deuterium oxide and also in aqueous dioxane. Substrate concentrations of 0.02 $M$ were used at 93°. The results are contained in Table V together with the results obtained in water under conditions which were otherwise the same. It was found that $k_H/k_D = 0.83 \pm 0.03$.

Table V

The Influence of Solvent on the Rate

| HCl, $M$ | Solvent | $k_1 \times 10^4$ Sec.$^{-1}$ |
|---|---|---|
| 0.0191 | 70:30 Dioxane–$H_2O$ | 2.45 |
| | $H_2O$ | 3.21 |
| .00956 | >97% $D_2O$[a] | 2.76[b] |
| | $H_2O$[a] | 2.29 |

[a] $\mu = 0.02$ obtained with NaCl. [b] Average of two runs with A.D.M. = $\pm 0.02 \times 10^{-4}$ sec.$^{-1}$.

**Temperature Dependence.**—The temperature dependence of the hydrolysis rate was investigated between 60° and 120° using 0.02 $M$ substrate and 0.00956 $M$ hydrochloric acid. Sodium chloride was used to obtain an ionic strength, $\mu = 0.02$. The results are recorded in Table VI. A plot of log $k_1/T$ *vs.* $1/T$ produced a straight line. The results were used to calculate the heat of activation, $\Delta H^\ddagger$, by the method of least squares from equation 2.[15]

$$\Delta H^\ddagger = 2.303[RTT'/(T - T')][\log k_1T'/k_1'T] \qquad (2)$$

$\Delta H^\ddagger = 18.2 \pm 0.9$ kcal./mole was obtained. From the usual thermodynamic relations the value $\Delta S^\ddagger = -16 \pm 2.5$ e.u. was calculated at 93°.[15] The uncertainties listed were computed using standard methods with 50% confidence limits.[16]

Table VI

The Hydrolysis Rate as a Function of Temperature

| Temp. | $k_1 \times 10^4$ Sec.$^{-1}$ |
|---|---|
| 59.9 | 0.163 |
| 76.6 | 0.637 |
| 93.1 | 2.29 |
| 99.5 | 3.72 |
| 110.5 | 7.84 |
| 120.0 | 13.7 |

## Discussion

In view of the fact that I is hydrolyzed in the presence of water alone and also exhibits a linear dependence upon the concentration of molecular acetic acid, $k_1$ of equation 1 must, in general, be of the form shown in equation, 3, where $k_0$ represents the rate constant for the "spontaneous" reaction with water.[17] In the case where acetic acid was employed at constant pH equation 3 reduces to $k_1 = \text{constant} + (\text{HA})\ [k_{HA} + k_{A^-}(\text{A}^-)/(\text{HA})]$. A plot of $k_1$ *vs.* (HA) should be linear of slope $= k_{HA} + k_{A^-}(\text{A}^-)/(\text{HA})$. The value of this slope is given in the last column of Table III for each of the two different buffer ratios used. The slopes are essentially the same in the two cases indicating that $k_{A^-}$ is sensibly zero and that the observed rate is due to unionized acetic acid or to its ions acting together.

$$k_1 = k_0 + k_{H^+}(\text{H}^+) + k_{OH^-}(\text{OH}^-) + k_{HA}(\text{HA}) + k_{A^-}(\text{A}^-) \qquad (3)$$

The results obtained here are consistent with a general acid-catalyzed hydrolysis. Catalysis by general bases must be small. Although the validity of the Brönsted relation[18] for the three acids, $H_3O^+$, acetic acid, and water is questionable because of the relatively large structural differences among them, a plot of log $k_A$ *vs.* log $K_A$ produced a fairly straight line of slope, $\alpha = 0.3$.[19] This suggests that the catalytic constant for any given acid is only moderately dependent on the dissociation constant of the acid.

The possibility for general acid catalysis in the hydrolysis of carboxylic acid derivatives has often

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[15] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 97.

[16] C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 38.

[17] R. P. Bell, "Acid-Base Catalysis," Oxford University Press, London, England, 1941, p. 60.

[18] Ref. 29, p. 82.

[19] The $k_A$'s were obtained at 93° and the $K_A$'s at 25°. Therefore, the value obtained for $\alpha$ should be viewed with some reservation.

been discussed.[2,11,20–26] However, the hydrolysis of I seems to be one of the few cases where this has been unequivocally established. It cannot be said whether the present example represents general acid catalysis in the classic sense[27] or whether this is an example of the electrophilic-nucleophilic catalysis discussed by Bender.[2,26] The finding of general acid catalysis in no way implies that the hydronium ion and general acid-catalyzed mechanisms must be the same.[28] If the general acid-catalyzed reaction proceeds by the same mechanism as the hydronium ion–catalyzed reaction, the observation of general acid catalysis alone requires that a water molecule be bound to the substrate in the transition state.

In the presence of hydrochloric acid equation 3 reduces to $k_1 = k_0 + k_{H^+}(H^+)$. The kinetic order with respect to hydrochloric acid appears to be distinctly less than one over much of the twenty-fold range in concentration employed. This behavior is illustrated in the third column of Table II. The tabulated values of $k_{H^+}$ result by straightforward calculation assuming a linear dependence of the rate on hydrochloric acid concentration. The measured rate of the "spontaneous" reaction with water has been taken into account in obtaining the listed values. It is clear that $k_{H^+}$ is not a constant. The nonlinearity with respect to acid is particularly apparent at the low acid concentrations below about 0.001 $M$. At higher concentrations $k_{H^+}$ is nearly constant and the apparent nonlinearity is not beyond the uncertainty in the measurements.

A less than linear dependence on acid and a rate maximum have been observed in a number of amide hydrolyses.[29–31] However, this has usually been found at acid concentrations above 1 $M$ and under conditions where the acid was in excess. Presumably, the amide becomes completely protonated as the acid concentration is raised and the further addition of acid serves only to lower the activity of water which is probably contained implicitly in the rate law.[2,29] This explanation does not seem applicable in the present case since the nonlinearity is more apparent at low concentrations, the acid was not in excess, and the concentrations employed were such that the activity of water should have been essentially constant.

The kinetic order of the reaction with respect to butyrolactam is one for all practical purposes as required by equation 1. This is illustrated by the constancy of $k_1$ in Table I. The slightly lower values of $k_1$ below 0.02 $M$ substrate may be due to small changes in the activity coefficients of the reactants as the medium is changed.

The change in rate accompanying the substitution of deuterium oxide for water as the solvent is in the same direction and of the same order of magnitude as observed for the acid hydrolysis of other carboxylic acid derivatives.[32] A finding of $k_H/k_D$ less than one is attributable to a mechanism in which substrate or an intermediate in equilibrium with substrate is reversibly protonated prior to the rate determining step.[32,33] The decreased rate with water is due to the lower equilibrium concentration of protonated species in water as compared to deuterated material in deuterium oxide. The fact that $k_H/k_D = 0.83$ rather than the value 0.3 predicted on this basis is probably due to the lower nucleophilicity of deuterium oxide compared to water.[2] This implies that the transition state contains a molecule of solvent as well as a proton covalently bonded to the substrate. The difference in nucleophilicities could either reflect itself in the rate-determining step or in an equilibrium prior to the rate-determining step. The observed solvent isotope effect explicity rules out the possibility that the rate-determining step is a proton transfer. The possibility that isotope effects may be caused by the change in medium has been pointed out.[34] The effect of a change in medium in the present reaction seems to be relatively small, however, since on changing the solvent from water to 70% dioxane the rate changes by less than a factor of two.

The heat and entropy of activation for the acid-catalyzed hydrolysis are of the same order of magnitude found in other reactions of this type.[2,35] The entropy of activation, $\Delta S^\ddagger = -16$ e.u., is consistent with a transition state which contains a water molecule in addition to a proton. Long[36] has generalized the data from a number of acid-catalyzed organic reactions and concluded that in those cases in which the transition state contains a water molecule plus a proton firmly bound to the substrate $\Delta S^\ddagger$ is of the order of $-20$ e.u. On the other hand, if only a proton is bound to the substrate in the transition state $\Delta S^\ddagger$ is small and may be either positive or negative.

The thermodynamics of activation and the solvent isotope effect were obtained at concentrations where the rate is practically linear in the acid concentration. These data are consistent with a transi-

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[20] H. M. Dawson and W. Lowson, *J. Chem. Soc.*, 2444 (1927).

[21] H. M. Dawson, E. R. Pycock, and E. Spivey, *ibid.*, 291 (1933).

[22] A. C. Rolfe and C. N. Hinschelwood, *Trans. Faraday Soc.*, **30**, 935 (1934).

[23] C. N. Hinschelwood and A. R. Legard, *J. Chem. Soc.*, 587 (1935).

[24] V. Gold and E. G. Jefferson, *ibid.*, 1409 (1953).

[25] M. L. Bender and B. W. Turnquist, *J. Am. Chem. Soc.*, **79**, 1652, 1656 (1957).

[26] M. L. Bender, *ibid.*, **79**, 1258 (1957).

[27] Ref. 29, p. 48.

[28] M. M. Kreevoy and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **77**, 3146 (1955).

[29] V. K. Krieble and K. A. Holst, *ibid.*, **60**, 2976 (1938).

[30] J. T. Edwards and S. C. R. Meacock, *J. Chem. Soc.*, 2000, 2007, 2009 (1957).

[31] T. W. J. Taylor, *ibid.*, 2741 (1930).

[32] K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

[33] Ref. 29, p. 143.

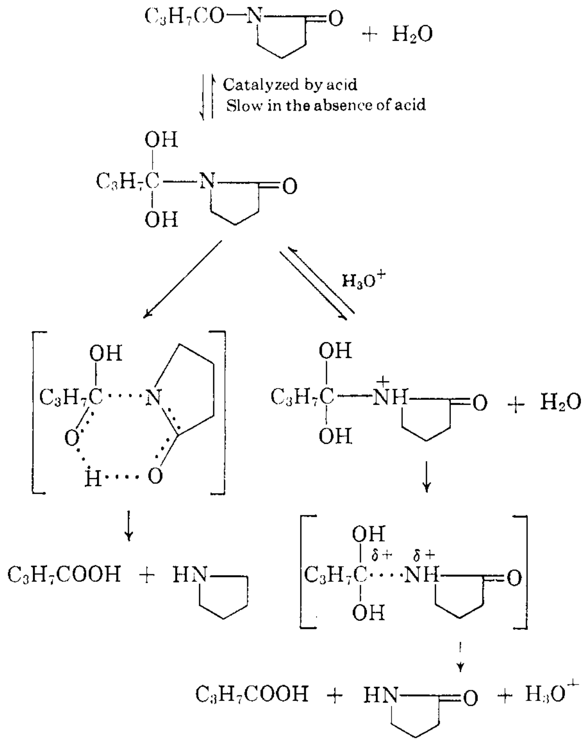
[34] E. A. Halevi, F. A. Long, and M. A. Paul, *J. Am. Chem. Soc.*, **83**, 305 (1961).

[35] K. J. Laidler, *ibid.*, **73**, 1712 (1951).

[36] F. A. Long, J. G. Pritchard, and F. E. Stafford, *ibid.*, **79**, 2362 (1957).

tion state containing a molecule of water and a proton in addition to the substrate. This is readily accommodated in a mechanism like that suggested by Bender.[2] However, at somewhat lower acid concentrations the striking nonlinearity with respect to acid concentration suggests that the reaction may be somewhat more complex.

The observed nonlinearity in acid at low acid concentrations may be explained by considering the probable effect of acid on the rate of the "spontaneous" reaction with water. It has been tacitly assumed to this point that the water reaction contributes a small constant fraction represented by $k_0$ to the over-all hydrolysis rate at *all* acid concentrations.



The formation of a tetrahedral hydrate in equilibrium with the starting material is a characteristic feature in the hydrolysis of carboxylic acid derivatives.[2] It seems likely that a hydrated intermediate is required for the water reaction as well as for that catalyzed by hydronium ion and is an intermediate common to both reactions. The hydrate normally results from nucleophilic attack at the carbonyl carbon atom followed by rapid proton transfer. Even in the presence of acid the formation of the hydrate can be so slow as to become the rate-determining step in some cases.[2] For the neutral water reaction, if the hydration and subsequent reaction of the hydrate have comparable rates the equilibrium concentration of the hydrate would not be attained during the course of the reaction. Acid should function effectively as a catalyst for the hydration equilibrium. Thus, in the presence of a catalytic amount of acid the concentration of the hydrate should be at or near the maximum value allowed by the equilibrium constant.

This will have an important effect on the kinetics observed in the acid-catalyzed hydrolysis if the rate of reaction is proportional to the hydrate concentration. When a small amount of acid is used $k_0$ will increase over the value determined in the absence of acid. This could not have been detected directly. At higher acid concentrations $k_0$ should then remain essentially the same. This will lead to the observation that the dependence of the rate on acid concentration is less than linear. At still higher acid concentrations the rate of the water reaction will be small compared with the rate of the acid-catalyzed reaction and a linear acid dependence will be observed.

The data in Table II were tested for this behavior by assuming that at the highest acid concentration the water reaction contributes nothing to the observed rate. This assumption establishes a value for $k_{H^+} = 1.65 \times 10^{-2}M.^{-1}\ sec.^{-1}$. Values of $k_0$ were then computed at each lower acid concentration. Four values were obtained and it was found that $k_0 = 0.54 \pm 0.18 \times 10^{-4}$/sec. where the uncertainty represents random scatter. Within the tabulated uncertainty the data are consistent with the view that the water reaction is catalyzed by acid in the manner discussed. The rate of the water reaction is increased ten-fold by a catalytic amount of acid and then remains constant when additional acid is used. Thus, the apparent nonlinearity with respect to acid is removed when the correct value for $k_0$ is used.

The reaction scheme which is presented embodies these principles. The mechanism by which molecular acetic acid catalyzes the hydrolysis remains undetermined.

**Acknowledgment.**—We are indebted to Professors M. M. Kreevoy and M. L. Bender as well as Dr. G. V. D. Tiers for stimulating discussions of this work.