$$R'-\overset{O}{\overset{\|}{C}}-O\overset{+}{H_2} \rightleftarrows R'\overset{O}{\overset{\|}{C}}-OH + H^+$$
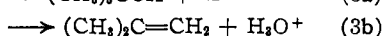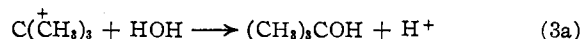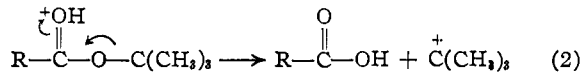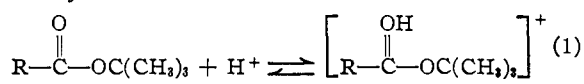
This series of reversible processes involves first a fast attachment of hydrogen ion to the alkyl oxygen atom of the ester, forming an oxonium ion. In a slow step, the electrophilic carbonyl atom of the oxonium ion is then attacked by a water molecule and a molecule of alcohol is expelled. The resulting oxonium ion rapidly loses a proton to form a carboxylic acid.

The PZ factor for the acid hydrolysis of t-butyl lactate is about 10^7 times larger than those for the other lactates, and the energy of activation is about 9 kcal./mole greater than the values for the remaining esters. Palomaa, et al.,[7] and Drushel and Dean[8] have measured rate constants for the acid hydrolyses of some alkyl acetates. Activation energies and PZ factors calculated from their data disclose that these values for the reaction involving t-butyl acetate exceed the values for the other acetic esters by about the same margin as that observed in our work on the lactic esters. It is therefore reasonable to assume that the mechanism for the acid hydrolysis of t-butyl esters is different from that which characterizes the acid hydrolysis of primary and secondary alkyl esters. Cohen and Schneider[9] have shown that t-butyl 2,4,6-trimethylbenzoate undergoes acid-catalyzed methanolysis by alkyl–oxygen fission and have reported evidence suggesting t-butyl esters suffer alkyl–oxygen fission on acid hydrolysis. Their mechanism for the alcoholysis is readily adapted to the hydrolysis of t-butyl esters.

$$R-\overset{O}{\overset{\|}{C}}-OC(CH_3)_3 + H^+ \rightleftarrows \left[R-\overset{OH}{\overset{\|}{C}}-OC(CH_3)_3\right]^+ \quad (1)$$

$$R-\overset{\overset{+}{O}H}{\overset{\|}{C}}-O\frown C(CH_3)_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + \overset{+}{C}(CH_3)_3 \quad (2)$$

$$\overset{+}{C}(CH_3)_3 + HOH \longrightarrow (CH_3)_3COH + H^+ \quad (3a)$$

$$\longrightarrow (CH_3)_2C{=}CH_2 + H_3O^+ \quad (3b)$$

This process involves the rapid reversible addition of a proton to the acyl oxygen atom of the ester, forming an oxonium ion which yields the carboxylic acid by the slow irreversible loss of the t-butylcarbonium ion. The latter may then be converted by water to t-butyl alcohol or through the loss of a proton to isobutylene; recent evidence[10] suggests that alcohol formation 3a should predominate over olefin formation 3b under the chosen conditions. It seems probable that steps 2 and 3 are not actually separate and distinct but are the components of a concerted process.

Comparison of the data for the acid hydrolyses of the n-alkyl lactates (Table I) and the data reported by Palomaa[7,11] and by Salmi[12] for the corresponding acetates demonstrates that increasing the length of the primary alkyl chain has little effect on the

(7) M. H. Palomaa. E. J. Salmi. J. I. Jansson and T. Salo, Ber., 68B, 303 (1935).

(8) W. A. Drushel and E. W. Dean, Am. J. Sci., 35, 486 (1913).

(9) S. G. Cohen and A. Schneider, THIS JOURNAL, 63, 3382 (1941).

(10) J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, ibid., 75, 1253 (1953); H. C. Brown and H. L. Berneis, ibid., 75, 10 (1953).

(11) M. H. Palomaa, Ann. Acad. Sci. Fennicae, A4, No. 2, 1 (1913).

(12) E. J. Salmi, Ber., 72B, 1767 (1939).

activation energy or the PZ factor for this reaction. However, sensible effects of chain branching may be observed. Branching by methyl at the β-position (isobutyl lactate) brings about an approximately tenfold increase in PZ, which is sufficient to cause a slight increase in the rate constants despite a simultaneous increase in E_a. Branching by methyl at the α-position (s-butyl lactate) likewise effects increases in both E_a and PZ; but in this case the former predominates, and the rate constants decrease. Substitution of a β-hydrogen atom in the ethyl group of ethyl lactate by a methyl, an ethyl, or a methoxy group brings about only very small progressive decreases in the velocity constants. Substitution by a β-chlorine atom brings about a somewhat larger decrease in rate, the result of an increased E_a.

The kinetic behavior of the four n-alkyl lactates on "neutral" hydrolysis (Table II) is in harmony with the assumption that the major reaction is really an acid hydrolysis in which the catalyzing acid is hydronium ion produced by the dissociation of the lactic acid formed during the reaction. However, the failure of the individual rate constants, E_a, and PZ values to agree with the values determined for the same compounds on acid hydrolysis suggests that the "neutral" hydrolysis is in fact a composite reaction of which the major component is acid hydrolysis but of which a hydrolysis reaction or reactions of some other type, possibly an internal displacement, also form a part. The anomalous behavior of n-butyl lactate in this series also suggests the operation of a competing hydrolysis reaction different from either acid or alkaline hydrolysis. Table II shows little change in velocity constants from methyl through n-propyl lactates on "neutral" hydrolysis. There is a progressive increase in both E_a and PZ through this series of compounds. However, the rate constants increase substantially in passing to n-butyl lactate, an effect caused largely by an increased PZ factor, as E_a is held constant. No such rate maximum for n-butyl lactate is found in either the acid or the alkaline hydrolysis.

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The Hydrolysis of Some Alkyl Lactates. III. Ethyl O-Acetyllactate and O-Acetyllactic Acid[1]

BY A. ALBERTO COLON, KENNETH H. VOGEL, ROBERT B. CARLIN AND J. C. WARNER

A number of investigations have been reported[2,3] on the kinetics of the hydrolysis of diesters in which the ester linkages are equivalent, but few studies have been made on diesters in which the linkages are not structurally equivalent. For this reason an investigation of the kinetics of the alkaline, acid and "neutral" hydrolyses of the diester, ethyl O-

(1) Abstracted from theses by A. A. Colon and K. H. Vogel presented to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the D.Sc. degree.

(2) C. K. Ingold, J. Chem. Soc., 133, 1375 (1930).

(3) J. Meyer, Z. physik. Chem., 67, 257 (1909).

acetyllactate, was undertaken. To help clarify the mechanism the rate of hydrolysis of O-acetyl-lactic acid also was studied. The results of these investigations are reported in this paper.

Materials and Method

Ethyl O-acetyllactate and O-acetyllactic acid, obtained from the Eastern Regional Laboratory of the United States Department of Agriculture,[4] were distilled under reduced pressure and stored in a desiccator over calcium chloride.

For ethyl O-acetyllactate: b.p. 175–177° (745.3 mm.), $n^{28}D$ 1.4051, sapn. equiv., 79.97; reported b.p. 177° (733 mm.),[5] $n^{17}D$ 1.4085,[5] calcd. sapn. equiv., 80.08.

For O-acetyllactic acid: b.p. 101° (1.5 mm.), $n^{20}D$ 1.4222, sapn. equiv., 131.45; reported b.p. 101° (1.8 mm.),[6] calcd. sapn. equiv., 132.06.

1,4-Dioxane (Paragon Purified Grade) was refluxed over sodium for 12 hours and distilled through a Hempel column.

The apparatus and experimental procedures for the alkaline. acid and "neutral" hydrolyses were identical with those described in the preceding papers of this series.[7,8]

For each alkaline hydrolysis of O-acetyllactate ion in dioxane–water solution, dioxane was weighed into the reaction flask by means of a torsion balance, accurate to ±0.05 g. A Victor Meyer bulb charged with a known amount of O-acetyllactic acid was placed in the flask, and sufficient water and standard sodium hydroxide solution were added to give the desired concentrations of O-acetyllactate ion and catalyzing base and to produce a solution of predetermined dielectric strength. Dielectric constants were taken from the data of Akerlof and Short.[9]
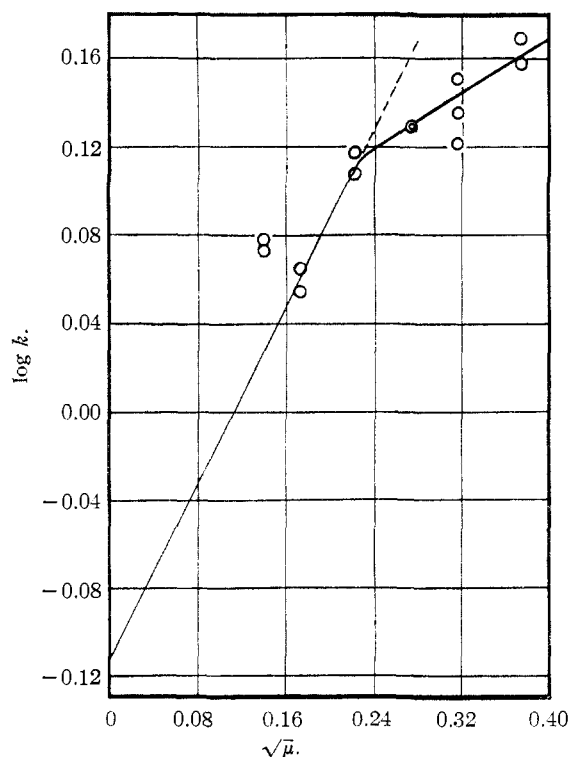

Fig. 1.—Rate constant as a function of ionic strength for alkaline hydrolysis of O-acetyllactic acid.

Alkaline Hydrolyses

Experimental Results.—Rate constants (all in liters mole^{-1} minute^{-1}) were calculated from the

(4) Courtesy of Drs. Lee T. Smith, C. H. Fisher and E. M. Filachione.

(5) L. T. Smith and H. V. Claborn, *Ind. Eng. Chem.*, **32**, 692 (1940).

(6) Drs. C. H. Fisher and E. M. Filachione, private communication.

(7) K. H. Vogel and J. C. Warner, THIS JOURNAL, **75**, 6072 (1953).

(8) A. A. Colon, K. H. Vogel and J. C. Warner, *ibid.*, **75**, 6072 (1953).

(9) G. Akerlof and O. A. Short, *ibid.*, **58**, 1241 (1936).

slopes of the best straight line plots of the data substituted into standard second order rate equations. Second order rate constants and activation energies for the alkaline hydrolysis of O-acetyllactate ion and for the two distinct steps of the alkaline hydrolysis of ethyl O-acetyllactate are summarized in Table I. The effect of changing ionic strength on the rate of the second step of the hydrolysis of ethyl O-acetyllactate is shown by a comparison of two rate constants determined in water solution at 40°. In solutions of ionic strengths 0.050 and 0.075, the respective average velocity constants were 1.862 and 2.549. A more detailed quantitative study of this effect was carried out in a series of alkaline hydrolyses of O-acetyllactate ion in water solution at 30°. The relationship between log k and $\mu^{1/2}$ is shown in Fig. 1. Table II summarizes the variation in the rate constant for the alkaline hydrolysis of O-acetyllactate ion with dielectric constant of dioxane–water solutions.
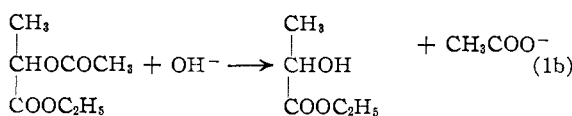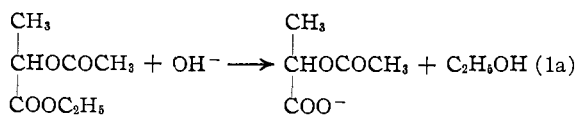
TABLE I

ALKALINE HYDROLYSES

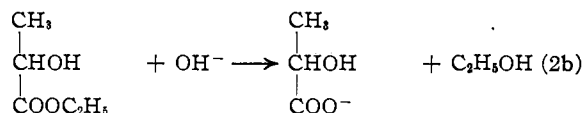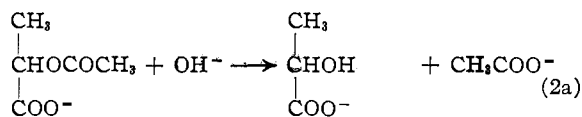| Ester	$k_0°$	$k_{10}°$	$k_{15}°$	$k_{40}°$	Ea, calcd.
Ethyl O-acetyllactate (1st step)	19.6	32.4			7,700
Ethyl O-acetyllactate (2nd step)	0.1018		0.3151	2.198	11,700
O-Acetyllactate ion	.1175		.3872	2.184	11,300

TABLE II

EFFECT OF DIELECTRIC CONSTANT ON THE RATE OF ALKALINE HYDROLYSIS IN SOLUTIONS OF CONSTANT IONIC STRENGTH ($\mu = 0.030$)

Dioxane, %	Dielectric constant	$k_{30}°$
7.64	70	1.105
19.10	60	1.090
30.64	50	1.005

Discussion of Results.—The rates of the two steps which make up the complete alkaline hydrolysis of ethyl O-acetyllactate differ so markedly that each can be measured readily. The kinetic data support the belief that the mechanism for the alkaline hydrolysis of ethyl O-acetyllactate and of O-acetyllactate ion, like that of other alkyl esters, involves the nucleophilic attack of hydroxyl ion on the carbonyl carbon atom followed by acyl oxygen fission.[7,10] Since the attack might occur at either of the two ester groups in the ethyl O-acetyllactate, both the reaction sequence 1a, 2a and the sequence 1b, 2b must be considered.

$$\begin{array}{l} CH_3 \\ | \\ CHOCOCH_3 + OH^- \longrightarrow \\ | \\ COOC_2H_5 \end{array} \quad \begin{array}{l} CH_3 \\ | \\ CHOCOCH_3 + C_2H_5OH \quad (1a) \\ | \\ COO^- \end{array}$$

$$\begin{array}{l} CH_3 \\ | \\ CHOCOCH_3 + OH^- \longrightarrow \\ | \\ COOC_2H_5 \end{array} \quad \begin{array}{l} CH_3 \\ | \\ CHOH \qquad + CH_3COO^- \\ | \qquad\qquad (1b) \\ COOC_2H_5 \end{array}$$

(10) J. N. E Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

$$CH_3 \qquad\qquad CH_3$$
$$|\qquad\qquad\qquad |$$
$$CHOCOCH_3 + OH^- \longrightarrow CHOH \qquad + CH_3COO^-$$
$$|\qquad\qquad\qquad |$$
$$COO^- \qquad\qquad COO^- \qquad\qquad\qquad (2a)$$

$$CH_3 \qquad\qquad CH_3$$
$$|\qquad\qquad\qquad |$$
$$CHOH \qquad + OH^- \longrightarrow CHOH \qquad + C_2H_5OH \quad (2b)$$
$$|\qquad\qquad\qquad |$$
$$COOC_2H_5 \qquad\qquad COO^-$$

Information previously available on the rates of alkaline hydrolysis of alkyl lactates and acetates pointed to reactions 1a and 2a as the more probable of the two sequences. One would expect the rate constant for reaction 1a to be approximately of the same order of magnitude as the known rate constant for reaction 2b (24.1 l. mole^{-1} min.$^{-1}$ at 15°)[8]; similarly, the rate constant for reaction 1b should not differ greatly from that for s-butyl acetate (0.816 l. mole^{-1} min.$^{-1}$ at 20°).[11] A comparison of these values with the rate constant for the first step in the alkaline hydrolysis of ethyl O-acetyllactate (Table I) strongly favors reaction 1a over 1b. Furthermore the small rate constants for the second step (Table I) eliminates 2b from consideration. Confirmatory evidence for reaction 2a was obtained by determining the rates and activation energies for the alkaline hydrolysis of O-acetyllactate ion (Table I) and comparing these quantities with analogous values for the second step.

The effect of changing ionic strength of the medium provides further evidence in support of the reaction sequence 1a and 2a. Strong positive salt effects both on the rate of the second step of the alkaline hydrolysis of ethyl O-acetyllactate and of that on the alkaline hydrolysis of O-acetyllactate ion were observed. The Brønsted–Bjerrum rate equation and the Debye–Hückel theory may be combined to yield the following equation[12] for water solutions at 25°

$$\log k = \log k_0 + 1.02 Z_A Z_B \mu^{1/2} \qquad (3)$$

where the Z terms are integers representing the charges on the ions A and B undergoing reaction, k and k_0 are the rate constants for a reaction measured in solutions of finite and infinite dilutions, respectively, and μ is the ionic strength of the former. This equation predicts a positive salt effect on the rate of a reaction such as 2a, which involves the interaction of two ions of like charge sign. The degree to which experimental data from the alkaline hydrolysis of O-acetyllactate ion approaches the limiting equation 3 is shown by Fig. 1. The straight line extrapolation to zero ionic strength in Fig. 1 has the theoretical slope 1.02, and the data appear to conform to a curve which approaches this straight line at lower ionic strengths.

Table II indicates a decrease in the rate of alkaline hydrolysis of O-acetyllactate ion with decreasing dielectric strength of the medium. This effect is to be expected of a reaction between two ions of like charge sign, in view of Scatchard's equation[13]

(11) H. Olsson, Z. physik. Chem., 118, 107 (1925).

(12) See S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941. p. 428.

(13) G. Scatchard, Chem. Revs., 10, 229 (1932).

$$\frac{\log k_0}{(1/D)} = - \frac{Z_A Z_B \epsilon^2}{2.303 r k T} \qquad (4)$$

where the Z terms and k_0 have the meanings assigned them in equation 3, D is the dielectric constant, ϵ is the unit electric charge, k is Boltzmann's constant, T is the absolute temperature and r is the radius of the activated complex. The rate constants (k) of Table II had to be transformed in some way to the corresponding rate constants at infinite dilution (k_0) before an effort could be made to apply equation 4. If the assumption is made that equations analogous to 3 hold for solutions having ionic strengths less than 0.030, then log k_0 values can be calculated from the k values of Table II, which were measured in solutions of ionic strength 0.030. In view of the comparatively small ionic strength of these solutions, the assumption is not likely to lead to gross errors. Figure 2 shows that a plot of log k_0 values, calculated in this way, against $1/D$ closely approximates the linear relationship predicted by equation 4. Since this equation indicates that the slope of the best straight line (Fig. 2) should be equal to $-Z_A Z_B \epsilon^2/2.303 r k T$, r, the radius of the transition state of reaction 2a, may be calculated as 8.1 Å. Compared with the distance of critical ionic separation for similar reactions,[14] this value seems too high even when one takes into account the uncertainty in extrapolating rate constants. Nevertheless, the observed effect of dielectric constant on rate qualitatively supports the proposed mechanism.
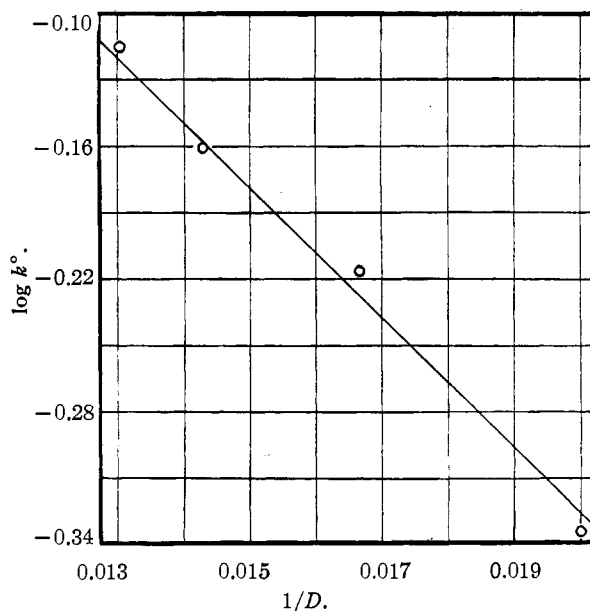

Fig. 2.—Rate constant extrapolated to zero ionic strength as a function of dielectric constant for alkaline hydrolysis of O-acetyllactic acid.

Acid Hydrolyses

Experimental Results.—Second-order rate constants (all in liters mole^{-1} minute^{-1}) for the acid hydrolyses of ethyl O-acetyllactate were evaluated from the slopes of the plots of log $(2a - x)$ vs.

(14) See E. A. Moelwyn-Hughes. "The Kinetics of Reaction in Solutions," 2nd edition, Oxford. Univ. Press, New York. N. Y., 1947, p. 106.

time in accordance with the pseudo first-order rate equation

$$k = \frac{-2.303}{ct} \log (2a - x) + \text{constant} \qquad (5)$$

in which a represents the initial concentration of ester, x the concentration of the resulting acid at time t, and c the essentially constant total acid concentration. The plots were linear up to conversions of about 70%, whereas log $(a - x)$ vs. time plots, according to the equation
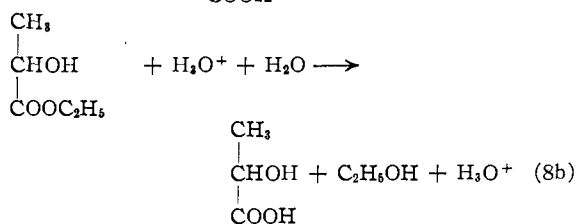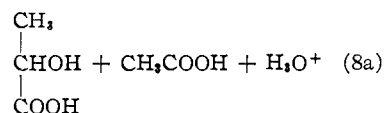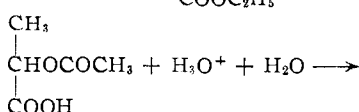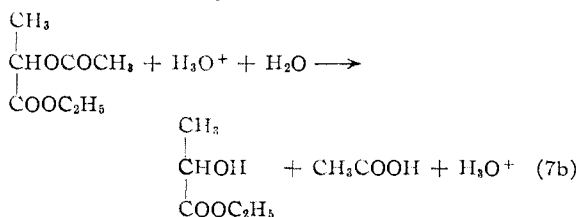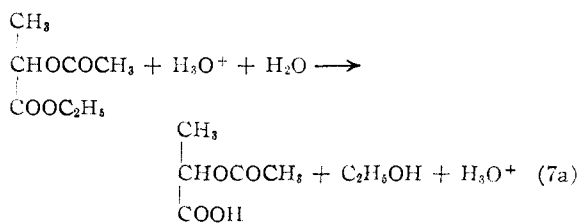
$$k = \frac{-2.303}{ct} \log (a - x) + \text{constant} \qquad (6)$$

were linear up to only 25–30% conversions. However, log $(a - x)$ vs. time plots were linear for the acid hydrolysis of O-acetyllactic acid to a high degree of conversion; accordingly the rate constants for this reaction were evaluated by means of equation 6. "Initial" rate constants for the acid hydrolysis of ethyl O-acetyllactate were computed from the slopes of the linear portions of plots of log $(a - x)$ vs. time, obtained at low conversions, and equation 6. Table III shows the rate constants and activation energies for the acid hydrolysis of ethyl O-acetyllactate and for the acid hydrolysis of O-acetyllactic acid.

TABLE III

ACID HYDROLYSES

Ester	k_{30} × 10^3	k_{40} × 10^3	k_{60} × 10^3	E_a Cal.
O-Acetyllactic acid		6.24	30.86	16,600
Ethyl O-acetyllactate	2.57	6.17	30.85	16,500
"Initial" rate ethyl O-acet-yllactate	5.41	13.82		17,700

Discussion of Results.—The kinetics of and the activation energies for the acid hydrolysis of ethyl O-acetyllactate and of O-acetyllactic acid indicate that the mechanism is the same as that which controls the acid hydrolysis of esters of primary alcohols.[8,10,15] Hydrolysis of ethyl O-acetyllactate might proceed by either of the routes 7a, 8a or 7b, 8b or by both simultaneously.

$$\underset{\underset{COOC_2H_5}{|}}{\overset{\overset{CH_3}{|}}{CHOCOCH_3}} + H_3O^+ + H_2O \longrightarrow$$

$$\underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{CHOCOCH_3}} + C_2H_5OH + H_3O^+ \qquad (7a)$$

$$\underset{\underset{COOC_2H_5}{|}}{\overset{\overset{CH_3}{|}}{CHOCOCH_3}} + H_3O^+ + H_2O \longrightarrow$$

$$\underset{\underset{COOC_2H_5}{|}}{\overset{\overset{CH_3}{|}}{CHOH}} + CH_3COOH + H_3O^+ \qquad (7b)$$

$$\underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{CHOCOCH_3}} + H_3O^+ + H_2O \longrightarrow$$

$$\underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{CHOH}} + CH_3COOH + H_3O^+ \qquad (8a)$$

$$\underset{\underset{COOC_2H_5}{|}}{\overset{\overset{CH_3}{|}}{CHOH}} + H_3O^+ + H_2O \longrightarrow$$

$$\underset{\underset{COOH}{|}}{\overset{\overset{CH_3}{|}}{CHOH}} + C_2H_5OH + H_3O^+ \qquad (8b)$$

The results of the kinetic studies support the belief that reactions 7a, 7b and 8a all proceed at essentially identical rates and have identical activation energies; reaction 8b has been studied previously[8] and is known to proceed at a rate about five times greater and to have an activation energy of about 3 kcal./mole less than the other three reactions. The function $(2a - x)$ measures the *concentration of all ester linkages* in solution; the function $(a - x)$ approximates the concentration of unchanged ethyl O-acetyllactate only during the early part of the reaction when nearly all of the ester linkages are present as unchanged ethyl O-acetyllactate. Therefore, the fact that log $(2a - x)$ is linear with time for a substantial portion of the reaction whereas log $(a - x)$ is linear with time only at low conversions indicates that the rate of acid hydrolysis of ester linkages of all types is being measured and all types of ester linkages being hydrolyzed are undergoing reaction at nearly identical rates, until high conversions are reached. The rate constants (Table III) for ethyl O-acetyllactate, derived from the log $(2a - x)$ plot, are in liters min.$^{-1}$ (*ester equivalent*)$^{-1}$; the initial rate constants, derived from the linear portions of the log $(a - x)$ vs. time plots, are in liters min.$^{-1}$ (*mole* of ethyl O-acetyllactate)$^{-1}$. Since the initial rates per mole are about twice those per ester equivalent, it is then reasonable to conclude that the two ester linkages of ethyl O-acetyllactate undergo acid hydrolyses (reactions 7a and 7b) at about the same rate and that the two reactions have about the same activation energy. It is also striking to observe (Table III) that the ester linkage of O-acetyllactic acid undergoes acid hydrolysis (reaction 8a) at the same rate and with the same activation energy as reactions 7a and 7b. If the foregoing deductions concerning the rates of reactions 7 and 8 are correct, then it follows that acetylation of the hydroxyl group of ethyl lactate causes about a fivefold decrease in rate of acid hydrolysis of the carbethoxyl group at room temperature and an increase of about 3 kcal./mole in activation energy (compare 8b and 7a). On the other hand esterification of O-acetyllactic acid with ethanol has no perceptible effect on the rate of acid hydrolysis of the acetoxyl group or on its activation energy. The activation energy is also virtually identical with the value 16,550 cal./mole calculated from the rate data of Palomaa, et al.,[16] on the acid hydrolysis of an analogous ester, s-butyl acetate.

The "neutral" hydrolysis of ethyl O-acetyllactate

(15) I. Roberts, Ann. N. Y. Acad. Sci., **39**, 375 (1940).

(16) M. H. Palomaa, E. J. Salmi, J. I. Jansson and T. Salo, Ber., **68B**, 303 (1935).

has been studied briefly and found to behave kinetically like the n-alkyl lactates. Therefore, the major reactions are again probably the hydronium ion-catalyzed hydrolyses of ester linkages, the hydronium ions being provided by the organic acids formed during the hydrolysis. Thus reactions 7 and 8 are doubtless concerned in the "neutral" hydrolysis in the same way that they are in the acid hydrolysis.

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Infrared Spectra and Structure of Crystalline Ammonia Hydrates

Recent very careful studies of the heat capacity and thermodynamic properties of $NH_3 \cdot H_2O$ and $2NH_3 \cdot H_2O$,[1] as well as earlier studies of the solid phases of the ammonia–water system,[2] have demonstrated that the two ammonia hydrates are well-defined compounds of exact composition.

The structure of these compounds is of some interest since they might exist either as simple hydrates or as ionic crystals. Although considerable experimental evidence exists to indicate that aqueous solutions of ammonia are only slightly ionized,[3] Hildenbrand and Giauque regard the crystalline hydrates as ammonium salts, i.e., $(NH_4)OH$ and $(NH_4)_2O$.

No previous spectroscopic studies of the solid phases of the NH_3–H_2O system were uncovered in a survey of the literature although the infrared and Raman spectra of aqueous ammonia[4,5] have been obtained.

In the present study mixtures of NH_3 and H_2O vapor were admitted to a low temperature infrared cell[6] and condensed on NaCl or KBr plates cooled with liquid nitrogen. The spectra obtained were consistent with an ammonia hydrate structure and definitely exclude an ionic structure.

Results

Figure 1 shows the spectra obtained for mixtures of NH_3 and H_2O at $-195°$, together with those of pure NH_3, H_2O and NH_4X for comparison. It is immediately clear that the spectra bear little resemblance to that of the $NH_4{}^+$ ion, and the absence of the $NH_4{}^+$ ion bending vibration at about 1400 cm.$^{-1}$ is conclusive. On the other hand, they closely parallel the spectra of crystalline NH_3 and H_2O, although there are some clear differences.

The interpretation of the low frequency region of the spectrum is most obvious. The strong ice band at 812 cm.$^{-1}$[7] appears in the spectrum with excess H_2O (A) but not in (B) or (C), so .that the

(1) D. L. Hildenbrand and W. F. Giauque. THIS JOURNAL, 75, 2811 (1953).

(2) I. L. Clifford and E. Hunter. J. Phys. Chem., 37, 101 (1933).

(3) P. F. van Velden and J. A. A. Ketelaar, Chem. Weekblad, 43, 401 (1947).

(4) G. Costeanu. R. Freymann and A. Naherniac. Compt. rend., 200, 819 (1935).

(5) B. P. Rao. Proc. Indian Acad. Sci., 20A, 292 (1944).

(6) E. L. Wagner and D. F. Hornig, J. Chem. Phys., 18, 296 (1950).

(7) F. P. Reding, Thesis, Brown University, 1951.

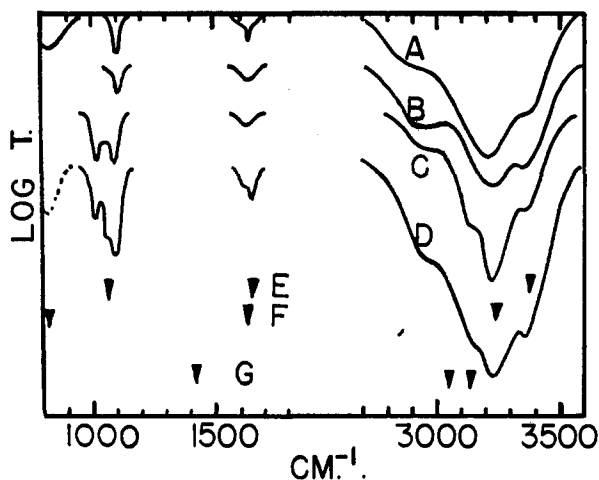Fig. 1.—Infrared spectra of crystals of the NH_3–H_2O system at $-195°$ together with comparison spectra: A, $NH_3 \cdot$-H_2O + H_2O; B, $NH_3 \cdot H_2O$; C, $2NH_3 \cdot H_2O$; D, NH_3 + $2NH_3 \cdot H_2O$ (some frost formation entailed by a small vacuum leak); E, crystalline NH_3; F, Ice; G, ammonium ion.

H_2O in the compounds is included in a lattice different from ice. If the 812 cm.$^{-1}$ band is a lattice vibration connected with the torsional oscillations of the H_2O molecules, the H_2O molecules cannot be as tightly bound in the hydrates as in ice; i.e., one of the O–H $\cdots$ O bonds must have been replaced by an O–H $\cdots$ N bond. The symmetrical bending vibration of ammonia, which occurs at 1060 cm.$^{-1}$ in the pure crystal,[8] appears at 1102 cm.$^{-1}$ in $NH_3 \cdot$-H_2O (B) and as a doublet, 1020 and 1091 cm.$^{-1}$, in $2NH_3 \cdot H_2O$ (C). The doubling probably indicates that the environment of the two NH_3 molecules is not identical. Excess NH_3 (D) produces an additional shoulder at 1069 cm.$^{-1}$ which may be identified as free NH_3.

Both the bending vibration of H_2O and the doubly degenerate bending vibration of NH_3 may contribute to the absorption near 1625 cm.$^{-1}$. However, since the symmetric bending vibration is far more intense than the degenerate one in both gaseous and crystalline NH_3, it does not seem likely that very much of the observed absorption in this region is caused by NH_3.

The stretching region cannot be analyzed so straightforwardly. The peak at 2950 cm.$^{-1}$ occurs in the spectrum of both hydrates but is relatively more intense in that of $NH_3 \cdot H_2O$ (B). It is probably too low in frequency to be ascribed to OH, since only acidic OH in very strong H-bonds absorbs at so low a frequency, and then only rarely. Similarly, NH $\cdots$ N bonds would probably not lead to such a low frequency, leaving an NH $\cdots$ O bond as the most likely explanation for this band. If this is correct, it seems likely that in $2NH_3 \cdot H_2O$ only one of the ammonia molecules is involved. The peak at 3140 cm.$^{-1}$ (C) belongs to $2NH_3 \cdot H_2O$ and may represent a weaker NH $\cdots$ O bond from the second NH_3 molecule.

The remaining peaks at 3220 and 3365 cm.$^{-1}$ are characteristic of hydrogen bonded O–H and N–H vibrations and cannot be assigned in detail. Although some of the 3220 cm.$^{-1}$ absorption in A is

(8) F. P. Reding and D. F. Hornig, J. Chem. Phys., 19, 594 (1951).