CXXX.—*The Mechanism of, and Constitutional Factors controlling, the Hydrolysis of Carboxylic Esters. Part II. Hydrolytic Stability Maxima of some Glyceric Esters.*

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IN selecting a method for the determination of catalytic data of the type of which the significance is discussed in Part I, our object was to combine wide applicability with some approach to accuracy.

The first consideration suggested the location of hydrolytic stability maxima, since, as has already been shown, this is the only method which remains practicable when strongly electron-attracting substituents adjoin the ester residue.

The second desideratum required that such a process be used only in conjunction with an adequate method for eliminating catalytic influences associated with the buffers used to define the p_H. These influences consist of (*a*) the superimposed catalysis of the buffer acid and buffer base, and (*b*) the effect of the buffer-ion environment on the activity of all the catalytic entities. A method for their elimination has been devised and is described later.

A third preliminary consideration was necessitated by the sparing solubility of the majority of esters, $R\cdot CO_2R'$, in water. The objections to the use of a mixed solvent, such as aqueous alcohol, for our purpose are obvious and are of a type not easy to surmount; it was therefore decided to avoid the difficulty by varying the radicals R and R′ separately and using a poly-hydroxylated group for the radical which is kept constant throughout any given series. In this paper, for example, we record the results obtained with a series of glyceric esters $CH_2(OH)\cdot CH(OH)\cdot CO\cdot OR$ (R variable).

Previous investigators who have undertaken experiments with the object of locating the hydrolytic stability maxima of esters in buffer solutions appear always to have aimed at using a sufficient buffer concentration to stabilise the p_H against disturbance from the acid liberated from the hydrolyte in the course of the experiment. This method involves two difficulties. First, the necessary concentration of buffer materials (which have to be neutralised in the course of the analytical work) is often such that the titre which measures the progress of hydrolysis is of the order of 1% of the total titre; and this sets a rather low limit to the accuracy obtainable in analysis. Secondly, in the present state of electrolytic theory there is no method for extrapolating to zero buffer concentration the velocity data obtained with concentrated buffer solutions, which is sufficiently trustworthy to obviate the necessity for an empirical check by reference to experimental data for low buffer concentrations; and this necessary empirical control is clearly impossible in a method in which, at the lowest buffer concentrations which are consistent with its principles, the buffer substances are still by far the main constituents of the solution. The first of these objections could, of course, be minimised by the use of gravi-volumetric methods of analysis; but since there seemed no way of overcoming the second, we rejected the method in favour of the following process.

An aqueous solution of the glyceric ester (concentration E_0) was treated with sufficient carbonate-free sodium hydroxide to hydrolyse a small proportion of it. At the temperature used, saponification occurred almost instantly with formation of sodium glycerate (concentration c), and in a few moments the solution passed through the neutral point and became faintly acid. It is easily seen that, from the moment of neutrality onwards, all effects on the dynamics of the reaction will be substantially the same as if sodium glycerate had been added at that moment to an ester solution of concentration $E = E_0 - c$. This sodium glycerate constituted the (constant) salt constituent of the buffer series, $c\mathrm{NaA} + x\mathrm{HA}$. The glyceric acid liberated in concentration x during the continuation of hydrolysis furnished the (variable) acid constituent of the buffer series, and also the measure of the decomposition of the hydrolyte.

In considering the dynamics of a hydrolysis subject to this kind of p_H control, it is convenient to treat effects (*a*) and (*b*) (see p. 1040) separately. First, we shall disregard effects due to buffer-ion environment. In symbolising the dynamics we shall follow the procedure developed by Dawson.

Application to the fundamental equation

$$v = v_{\mathrm{H}} + v_{\mathrm{OH}} + v_m + v_a + v_w = k_{\mathrm{H}}[\mathrm{H}^{\cdot}] + k_{\mathrm{OH}}[\mathrm{OH}'] + k_m[\mathrm{HA}] + k_a[\mathrm{A}'] + k_w[\mathrm{H_2O}]$$

of the mass-law relations

$$[\mathrm{A}'] = c + [\mathrm{H}^{\cdot}] \text{ and } [\mathrm{HA}] = c[\mathrm{H}^{\cdot}]/K + [\mathrm{H}^{\cdot}]^2/K \quad . \quad (1)$$

leads to

$$v = \left(k_{\mathrm{H}} + \frac{k_m c}{K} + k_a\right)[\mathrm{H}^{\cdot}] + \frac{k_{\mathrm{OH}}K_w}{[\mathrm{H}^{\cdot}]} + \frac{k_m}{K}[\mathrm{H}^{\cdot}]^2 + (k_a c + k_w[\mathrm{H_2O}]) \quad (2)$$

of which

$$v = \left(k_{\mathrm{H}} + \frac{k_m c}{K}\right)[\mathrm{H}^{\cdot}] + \frac{k_{\mathrm{OH}}K_w}{[\mathrm{H}^{\cdot}]} + (k_a c + k_w[\mathrm{H_2O}]) \quad . \quad (3)$$

is an approximate form. The approximation consists in the neglect of $[\mathrm{H}^{\cdot}]$ in comparison with c, and so long as the former is of the order $10^{-4\cdot5}$ and the latter of order 10^{-1} this is justifiable. The quantities, $v = u$ and $[\mathrm{H}^{\cdot}] = h$, characterising the relation $dv/d[\mathrm{H}^{\cdot}] = 0$ are given by

$$u = 2\left\{k_{\mathrm{OH}}K_w\left(k_{\mathrm{H}} + \frac{k_m c}{K}\right)\right\}^{\frac{1}{2}} + (k_a c + k_w[\mathrm{H_2O}]) \quad . \quad (4)$$

and

$$h = \left\{k_{\mathrm{OH}}K_w\middle/\left(k_{\mathrm{H}} + \frac{k_m c}{K}\right)\right\}^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad (5)$$

and, if w is written for that part of v which is independent of $[\mathrm{H}^{\cdot}]$, the approximate equation (3) for v takes a form equivalent to that used by Dawson to express the symmetry of the v–p_{H} relation, *viz.*,

$$2\frac{v-w}{u-w}=\frac{[\mathrm{H}^{\cdot}]}{h}+\frac{h}{[\mathrm{H}^{\cdot}]} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

In using this form for the purpose of deriving an equation for the experimentally determined x–t relation, we should substitute for v and $[\mathrm{H}^{\cdot}]$, using

$$dx/dt = v(E-x) \quad . \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

and

$$K(x-[\mathrm{H}^{\cdot}]) = [\mathrm{H}^{\cdot}](c+[\mathrm{H}^{\cdot}]) \, . \quad . \quad . \quad . \quad . \qquad (8)$$

but if the second of these equations is replaced by $[\mathrm{H}^{\cdot}] = Kx/c$, the approximation (except at the commencement of the reaction) is of the same order as that introduced above, and the differential equation takes the comparatively simple form

$$\frac{dx}{dt} = (E-x)\left\{\tfrac{1}{2}(u-w)\left(\frac{Kx}{hc}+\frac{hc}{Kx}\right)+w\right\} \quad . \quad . \qquad (9)$$

The manner in which the solution of equation (9) should be expressed in order that it may be real depends on the relative magnitudes of u and $2w$. In our experiments u was always greater than $2w$, and the real form of the solution for this case is

$$t\left\{\frac{E^2K^2}{h^2c^2}+\frac{2EKw}{(u-w)hc}+1\right\} = EK\log_e\left[\frac{E}{E-x}\left\{\frac{K^2x^2}{h^2c^2}+\frac{2Kwx}{(u-w)hc}+1\right\}\right]$$
$$-\frac{(u-w)hc-EKw}{\sqrt{u^2-2uw}}\left\{\tan^{-1}\frac{\dfrac{(u-w)Kx}{hc}+w}{\sqrt{u^2-2uw}}-\sin^{-1}\frac{w}{u-w}\right\} \quad (10)$$

From numerical data conforming to this equation it is obviously possible to construct the curve of equation (3) or its equivalent (6), and also the (dx/dt)–x curve (equation 9).

It is now necessary to consider the effect of varying c. Since, for a given value of $[\mathrm{H}^{\cdot}]$, equation (2) may be written

$$v = A + \left(\frac{k_m[\mathrm{H}^{\cdot}]}{K}+k_a\right)c \, . \quad . \quad . \quad . \quad . \qquad (11)$$

it follows that, in so far as the mass law expresses the situation, v is a linear function of c for constant $[\mathrm{H}^{\cdot}]$, and dv/dc is a linear function of $[\mathrm{H}^{\cdot}]$. If, therefore, we use a family of experimentally obtained x–t curves to plot a corresponding family of v–$[\mathrm{H}^{\cdot}]$ curves, and then employ them to construct a family of v–c curves, the last should be straight lines. Their intercepts on the axis $c = 0$ should yield the data required for the construction of a v–$[\mathrm{H}^{\cdot}]$ curve corresponding with $c = 0$, and their slopes should give a (dv/dc)–$[\mathrm{H}^{\cdot}]$ curve, of which the slope measures k_m/K and the intercept on the axis $[H^{\bullet}] = 0$ measures k_a. The mass-law expression for the $(v\text{–}[H^{\bullet}])_{c=0}$ curve is

$$v_0 = (k_H + k_a)[H^{\bullet}] + \frac{k_{OH}K_w}{[H^{\bullet}]} + \frac{k_m}{K}[H^{\bullet}]^2 + k_w[H_2O]. \quad (12)$$

but the practical simplification which results from applying the above procedure to our experimental data is greater still, because, although only rough estimates of k_a and k_m are possible, it transpires that k_a/k_H is of the order 10^{-4}, and that in the neighbourhood of the stability maximum $k_m[H^{\bullet}]/K$ is of the same order as k_a; that is, there are reasons, justifying the omission of the terms $k_a[H^{\bullet}]$ and $k_m[H^{\bullet}]^2/K$ from equations (2) and (12), which are independent of the reason that applies in the case of equation (2) when c is great in comparison with $[H^{\bullet}]$; the last reason therefore still holds good when $c = 0$, and the equation for the v_0–$[H^{\bullet}]$ curve may be expressed

$$v_0 = k_H[H^{\bullet}] + \frac{k_{OH}K_w}{[H^{\bullet}]} + k_w[H_2O] \quad . \quad . \quad . \quad (13)$$

If w_0 is written for $k_w[H_2O]$, the corresponding data for the stability maximum in the absence of buffer substances are

$$u_0 = 2\sqrt{k_H k_{OH} K_w} + w_0 \quad . \quad . \quad . \quad . \quad (14)$$

$$h_0 = \sqrt{k_{OH}K_w/k_H} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

and, in terms of these quantities, the equation for v_0 is

$$2\frac{v_0 - w_0}{u_0 - w_0} = \frac{[H^{\bullet}]}{h_0} + \frac{h_0}{[H^{\bullet}]} \quad . \quad . \quad . \quad . \quad (16)$$

The above outline of the method we have adopted in order to eliminate from our results effects due to the catalytic activity of the constituents of the buffers, leaves untouched the question of correcting for disturbances due to the effect of ion-environment on catalytic activity. Brönsted, in particular, has drawn attention to the importance of these influences in homogeneous catalysis. Now, Dawson and his collaborators have also envisaged this problem, and, although we must agree with Brönsted that recognition of the disturbances mentioned is equivalent to an admission that mass-law relations are inapplicable, what is of more importance is that Dawson has found a simple method of giving a quantitative account of the actual catalytic relations; and his method may be expressed in the statement that the *form* of the mass-law equations holds good provided that the coefficients are no longer regarded as constants, but are replaced by suitable *functions of the ionic strength.* Dawson and Key, for instance, investigated the effect of neutral salts on the catalysis of the iodination of acetone (J., 1928, 1248), and found that, with one exception, the deviations from constancy which it was necessary to ascribe to the catalytic coefficients were barely detectable. For the one coefficient (namely, k_H) for which the variation could be measured, it was found to be represented by a linear function of the ionic strength over a very much greater range of ionic strength than any with which we are concerned. It can readily be shown (i) that, if conditions which are similar in regard to the orders of magnitude of the quantities involved hold also for ester hydrolysis, then the main effect on the relations which equation (11) purports to express will be represented by an alteration in the slope of the v–c curves (because, of course, A contains k_H); and (ii) that the variations attributable to k_m and k_a are unlikely in practice to impart any perceptible curvature to these graphs within the range of concentration used in our experiments. Again, Dawson and Lowson have made a study of salt effects on the hydrolysis of ethyl acetate in which they have considered especially the deviations with increasing salt concentration which must be ascribed to the dissociation constants of weak acids (J., 1929, 1217). They found that the variability with which it is necessary to credit these constants is of the type required by the Debye–Hückel theory of electrolytes, although there remained a divergence from that theory in the matter of the numerical value of one of the constants of the equation connecting K with c. The effect of influences of this nature on the relations which equation (11) is supposed to represent can be qualitatively deduced, although they are somewhat complicated. There will be, for instance, an effect on the explicit K; this is calculated to impart to the v–c curves a convexity towards the c-axis, which might be large enough to be perceptible on the acid side of the stability maximum, but would be extremely slight on the alkaline side. On the other hand, there will be an indirect effect on v arising from the fact that v is a function of [H$^{\cdot}$], which is a function of K; and this should produce a slight convexity towards the c-axis on the acid side of the stability maximum. Similarly, opposing effects, relating primarily to the alkaline side of the stability maximum, can be foreseen; and the general conclusion which emerges from a consideration of the probable orders of magnitude of the quantities involved is that the main effect of the disturbances considered would again be represented by an alteration of the slope of the v–c curves, although small departures from linearity remain theoretically possible. Further details with regard to the theoretical aspect of this matter need not be discussed, because we find that, for the range of salt concentration employed, the v–c curves are, in fact, straight lines to within the limits of consistency of the data. It is, therefore, clear that the process of linear extrapolation outlined above must yield velocity values (v_0) which are not only independent of contributory catalysis by the buffer constituents, but are also free from the disturbing effects of buffer-ion environment on catalytic activity; in other words, the v_0–[H$^\bullet$] curve obtained from the experimental data by the method indicated should be represented, to a degree of accuracy determined only by the data themselves, by equations (13—16), in which all the quantities pertain to salt-free aqueous solutions.

There is one disturbing factor which cannot be eliminated by any such method as that outlined, and that is the effect of the ester itself in modifying the properties of the aqueous medium. Knowing nothing about this, we have been forced to neglect it; but inasmuch as it is proposed later to compare the results obtained, we have endeavoured to arrange that effects due to the ester shall be kept as nearly constant as possible throughout the series by using, in every case, solutions of uniform ester concentration.

Eight esters of *dl*-glyceric acid with alcohols of simple constitution have been examined by the method described. The results are summarised in Section E of the experimental part of this paper (see especially Table IX and Figs. 4 and 5). Discussion of the data is postponed until the results of further experiments, now in progress, are available for collective consideration.

EXPERIMENTAL.

(A) *Materials.*—*dl*-Glyceric acid was prepared by oxidation of glycerol with nitric acid ("Beilstein," 4th Aufl., III, 395). Its esters with aliphatic alcohols have hitherto usually been obtained by heating the acid with the alcohol at 180—190° (Frankland and McGregor, J., 1893, **63**, 512; Frankland and Price, J., 1897, **71**, 253), but we found that esters prepared by this method turned brown on keeping. The esters were therefore prepared by boiling the acid (it is not necessary that it should be absolutely anhydrous) with an excess of the alcohol containing 1% of hydrogen chloride. Careful fractionation under diminished pressure yielded stable, colourless esters of constant b. p., which, however, contained traces of chlorine compounds. These were removed by distillation under reduced pressure with freshly prepared silver oxide. The esters appeared to be somewhat hygroscopic, and, accordingly, precautions were taken to prevent access of moisture. Purity was checked by quantitative saponification (G = glyceryl group). The italics in Table I indicate the esters which are new.

(B) *Calibration.*—In order to obtain a convenient rate of reaction in the neighbourhood of the stability maxima it was found necessary to use a temperature considerably above that of the room. Since

TABLE I.

dl-Glycerate.	B. p.	G (found), %.	G (calc.), %.
Methyl	123—125°/10 mm.	74·16, 74·00	74·20
Ethyl	126·5°/10 mm.	66·50, 66·60	66·40
n-Propyl	128—129°/10 mm.	60·13	59·94
iso*Propyl*	126—127°/11 mm.	59·87	59·94
n-Butyl	127—129°/10 mm.	54·72	54·91
*iso*Butyl	117°/9 mm.	54·86	54·91
n-*Amyl*	134—136°/11 mm.	50·43	50·56
iso*Amyl*	135—137°/11 mm.	50·45	50·56

the titrations were carried out at room temperature, the ordinary methods for the intercalibration of volumetric apparatus were inapplicable on account of thermal expansion. We therefore standardised the barium hydroxide solution used for the acidimetric measurements by a method which included an automatic relative calibration of the series of flasks and pipettes used against the already internally calibrated burette. The procedure may be illustrated as follows.

Pure succinic acid (1·2832 g.) was placed with distilled water in a flask, A, which had a mark on the neck, and the solution was made up with water to the mark at 70·2°. At this temperature a sample was withdrawn with a nominally 25 c.c. pipette, (a), and titrated, in the presence of an approximately standard quantity of phenolphthalein, with nominally $N/40$-barium hydroxide, 39·38 ml. of which were required to produce the tint which throughout these experiments was accepted as an indication of the end-point. The capacity of the flask, up to its mark, at the same temperature, was determined gravimetrically, allowance being made for the buoyancy of water in air, and found to be 539·2 ml. It follows that each ml. of titre corresponds with the presence of 0·0010265 g.-equiv. of acid per litre in a solution the sample of which has been withdrawn at the temperature stated from flask A by pipette (a). This temperature was used throughout the velocity measurements. Flasks B—F were treated similarly in relation to pipette (a); later, another set G—K were treated likewise in relation to a second pipette (b).

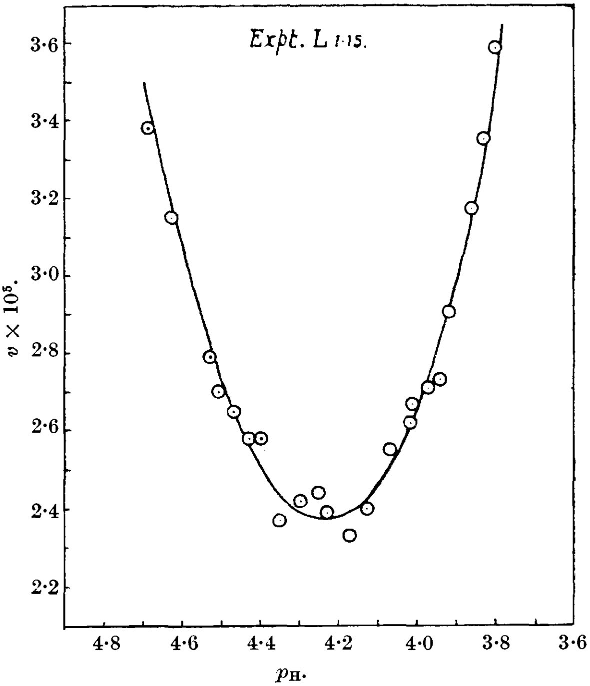
(C) *Details of a Typical Experiment* (Expt. L, 1·15).—A mixture of methyl glycerate (see Table I) (42·004 g.), warm distilled water (about 400 c.c.), and 0·9746N-sodium hydroxide (83·01 ml.) in flask A was placed in the thermostat, and, after temperature equilibrium had been attained, the whole was made up to the mark. At intervals extending over about a week, samples were withdrawn with pipette (a) and titrated in the manner described in Section B. The results are given in the 2nd, 3rd, and 4th columns of Table II, t being the time (in minutes) and x the normality of the acidity.

TABLE II.

Observation No.	*t*.	Titre, ml.	*x*.	*t* (calc.).	Deviation in *t*.
1	271	10·74	0·01102	(271)	
2	390	12·75	0·01309	392	− 2
3	562	15·41	0·01581	563	− 1
4	714	17·55	0·01802	714	± 0
5	1075	22·10	0·02268	1068	+ 7
6	1395	25·92	0·02660	1398	− 3
7	1668	29·13	0·02990	1676	− 8
8	1887	31·25	0·03208	1877	+10
9	2165	34·54	0·03545	2167	− 2
10	2806	41·32	0·04241	2812	− 6
11	3228	45·67	0·04688	3226	+ 2
12	3651	50·11	0·05144	3650	+ 1
13	4345	57·77	0·05930	4348	− 3
14	4802	62·86	0·06452	4798	+ 4
15	4998	65·16	0·06688	4999	− 1
16	5744	73·60	0·07556	5734	+10
17	6222	79·29	0·08141	6217	+ 5
18	7105	90·38	0·09277	7105	± 0
19	7615	96·94	0·09951	7620	− 5
20	8359	107·19	0·11003	8374	−15

From the data given it can be calculated that $E = 0{\cdot}4988$ and $c = 0{\cdot}1500$. The times recorded in the 5th column of Table II are calculated from an equation equivalent to (10), the values used being $K = 2{\cdot}28 \times 10^{-4}$, $u = 2{\cdot}37 \times 10^{-5}$, $w = 0{\cdot}37 \times 10^{-5}$, and $h = 8{\cdot}81 \times 10^{-5}$. The value of K is taken from Ostwald's measurements at 25° (*Z. physikal. Chem.*, 1889, **3**, 192), and its selection is admittedly arbitrary, because, apart from other considerations (see below), the temperature is not that of our experiments. No determinations of K appear to have been made at higher temperatures, and we have not attempted to introduce a temperature correction by means of special experiments, for the following reasons. First, judging from such evidence as is available, the thermal variations in the dissociation constants of simple monocarboxylic acids are so slight that they are difficult to estimate with accuracy, either from conductivities, or from heats of neutralisation, except on the basis of an elaborate investigation. Secondly, the correction, if it could be estimated, would probably be smaller than the uncertainty in the value for the basic temperature, 25°; Böeseken, for instance, records $2{\cdot}8 \times 10^{-4}$ for this temperature (*Rec. trav. chim.*, 1918, **37**, 169). Thirdly, as is pointed out in the introduction, our experiments are necessarily affected by the circumstance that our buffer-free solvent is, not water, but an aqueous solution of the ester; whilst this disturbing influence inevitably affects K (and there is no point in attempting to eliminate it, since the same cannot be done for the other coefficients and constants involved), it would be superfluous to endeavour to eliminate from K the (probably smaller) disturbance due to temperature. In the circumstances, the best course seemed to be to adopt a definite value of K and keep to it throughout the work; and since the effects mentioned would probably tend to reduce K, we have chosen the lower of the two recorded values. Errors due to an incorrect value of K should, we think, be constant throughout the series of experiments, because, as has been explained, all effects (including the one on K) due to the main *variable* factor, namely, the salt concentration, are eliminated during the reduction of our results to those which should pertain to the buffer-free medium. The x–t curve plotted from the figures in Table II runs generally upwards and to the right, but contains a point of inflexion (minimal slope) in the neighbourhood of the 10th observation. Of the three values u, w, and h selected to give that degree of agreement with equation (10) which is indicated in the 6th column, u is mainly responsible for the general slope, w controls the degree of acuteness of the inflexion, and h its position. It should be added that, since there is a certain indefiniteness about the time of starting, and also because the integrated formula is not accurate near the commencement of the reaction, the first observation was treated as the effective

FIG. 1.



starting point for computation; * this is indicated by the parenthesis at the top of the table.

The general nature of the x–t relation can be more clearly exhibited by using the differences between neighbouring observations to calculate v from equation (7) and the means of such observations to obtain corresponding values of $[\text{H}^{\bullet}]$ (or p_H) from equation (8). The results of this calculation are given in Table III, the figures in the last two columns of which are graphically represented in Fig. 1.

In the table, col. 1 enables the pair of observations used to be identified in Table II; cols. 2 and 3 record respectively the differences of time and of acidity; col. 4 gives the mean acidity for each interval; and cols. 5 and 6 record the mean molecular concentrations of glyceric acid and of glyceric ester for each interval. It will be seen that only about one-fifth of the total possible reaction has been followed (in the majority of our experiments the fraction is smaller), and for this reason, having regard to Dawson and Lowson's investigation of the effect of reversibility on the dynamics of the hydrolysis of ethyl acetate (J., 1927, 2107), we need not fear serious disturbance from the retrograde reaction.

TABLE III.

Nos.	Δt.	Δx.	x (mean).	$x - [\text{H}^{\bullet}]$.	$E - x$.	$v \times 10^5$.	p_H.
1—3	291	0·00479	0·0134	0·0134	0·4854	3·38	4·69
2—4	324	0·00493	0·0155	0·0155	0·4833	3·15	4·63
3—5	513	0·00687	0·0192	0·0192	0·4796	2·79	4·53
4—5	362	0·00466	0·0203	0·0203	0·4785	2·70	4·51
4—6	681	0·00858	0·0223	0·0223	0·4765	2·65	4·47
5—6	320	0·00392	0·0247	0·0247	0·4741	2·58	4·43
5—7	593	0·00722	0·0263	0·0263	0·4725	2·58	4·40
6—8	492	0·00548	0·0293	0·0293	0·4695	2·37	4·35
7—9	497	0·00555	0·0327	0·0326	0·4661	2·42	4·30
8—10	919	0·01033	0·0372	0·0371	0·4616	2·44	4·25
9—10	641	0·00706	0·0390	0·0389	0·4598	2·39	4·23
10—11	422	0·00447	0·0446	0·0445	0·4542	2·33	4·17
11—12	420	0·00456	0·0492	0·0491	0·4496	2·40	4·13
12—13	694	0·00786	0·0554	0·0553	0·4434	2·55	4·07
13—14	457	0·00522	0·0619	0·0618	0·4369	2·62	4·02
13—15	653	0·00758	0·0631	0·0630	0·4357	2·67	4·01
14—16	942	0·01104	0·0700	0·0699	0·4288	2·71	3·97
15—16	746	0·00868	0·0712	0·0711	0·4276	2·73	3·96
16—17	478	0·00585	0·0785	0·0783	0·4203	2·90	3·92
17—18	883	0·01136	0·0921	0·0919	0·4067	3·17	3·86
18—19	500	0·00674	0·0961	0·0959	0·4027	3·35	3·83
19—20	744	0·01052	0·1047	0·1045	0·3941	3·58	3·80

It will be obvious from Fig. 1 that the experimental data correspond with a curve approximating more or less closely to the usual

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* To do this we replace t (equation 10) by $t - t_1$, remove the term $\sin^{-1}$ (an integration constant), and subtract from the right-hand side of the residual equation an expression identical with that side except that x_1 replaces x, (x_1, t_1) being the first observation.

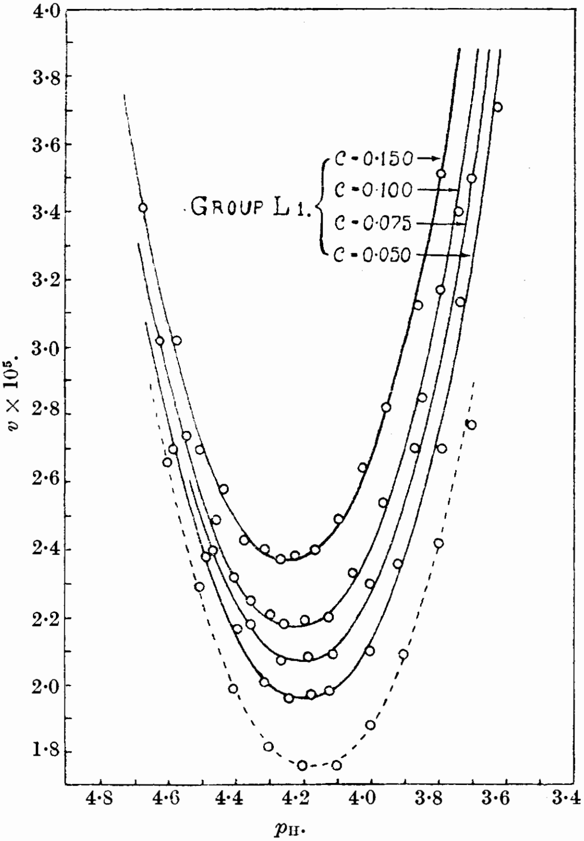
catenary form ; the main purpose of the figure, however, is to exhibit the fact that the accuracy of the individual observations is insufficient to enable directly read differences to define the v–p_H curve with any approach to precision (the curve drawn is constructed as described below). Our practice in this and the other experiments has therefore been to plot the x–t observations, and to read dx/dt from the curve. We regard this method of eliminating the casual errors of individual observations as allowable because it is a close graphical analogue to many accepted legitimate methods of attaining the same end, as, for instance, the averaging of a column of individually calculated velocity coefficients derived by the application of an integrated formula to a series of observations tracing the progress of a reaction; indeed, the latter process is, if anything, more difficult to defend because integration itself involves an averaging of errors which might seriously affect direct application of the data to the differential equation to which they should correspond. In applying the graphical process indicated, we found it convenient to plot $1000x \cos \theta - 0{\cdot}01t \sin \theta$ against $100x \sin \theta + 0{\cdot}001t \cos \theta$, where θ is an angle shown to be suitable by a preliminary rough plot of x against t. This method avoids the use of an inconveniently extended scale; the effect is much as if the x–t data were plotted on a sheet of rubber which was then stretched 10-fold in a direction at right-angles to the general direction of the curve in order to bring into relief the deviations of the points from the curve. For the experiment now considered 45° is a suitable value for θ. Proceeding in this way, we obtained the data shown in Table IV, the headings of the first five columns of which are self-explanatory. The velocity values in col. 6 are calculated from equation (6) by use of the values of u, w, and h given above. Col. 7 shows the deviations, which are seen to be small and casual in character.

TABLE IV.

				$v \times 10^5$.		
x.	$10^5 . dx/dt$.	p_H.	$E - x$.	Found.	Calc.	Diff.
0·0141	1·653	4·67	0·4847	3·41	3·41	±0·00
0·0177	1·453	4·57	0·4811	3·02	2·98	+0·04
0·0208	1·290	4·50	0·4780	2·70	2·73	−0·03
0·0246	1·224	4·43	0·4742	2·58	2·56	+0·02
0·0281	1·144	4·37	0·4707	2·43	2·46	−0·03
0·0315	1·121	4·31	0·4673	2·40	2·39	+0·01
0·0382	1·045	4·26	0·4606	2·37	2·37	±0·00
0·0400	1·046	4·22	0·4588	2·38	2·37	+0·01
0·0454	1·088	4·16	0·4534	2·40	2·40	±0·00
0·0541	1·108	4·09	0·4447	2·49	2·48	+0·01
0·0621	1·153	4·02	0·4367	2·64	2·62	+0·02
0·0725	1·201	3·95	0·4263	2·82	2·82	±0·00
0·0924	1·268	3·86	0·4064	3·12	3·17	−0·05
0·1065	1·377	3·79	0·3923	3·51	3·52	−0·01

The data in the third and fifth columns enable the v–p_H curve to be located to within $\pm 0{\cdot}01$ unit of p_H and of $v \times 10^5$, except at a distance from the stability maximum where the uncertainty of v is somewhat greater. The curve is practically symmetrical about the ordinate $p_H = 4{\cdot}24$.

FIG. 2.



(D) *Summary of a Typical Group of Experiments* (Group L1).—This group consists of four experiments of the same nature as that particularised in Section C. 0·5*M*-Methyl glycerate (*E*) was employed throughout, but the concentration of sodium glycerate (*c*) was different in each experiment, being 0·050 in the first, 0·075 in the second, 0·100 in the third, and 0·150 in the fourth. The second experiment was carried out about a year before the other three, which were done contemporaneously; this is mentioned in order to show that during the rather long period over which the measurements recorded in this paper have extended, a satisfactory constancy of conditions has been maintained.

Proceeding as described in the previous section, we obtained the values of v and p_H shown in Table V. The plot of these results is exhibited in Fig. 2 (full-line curves).

TABLE V.

$c = 0·050$.		$c = 0·075$.		$c = 0·100$.		$c = 0·150$.	
p_H.	$10^5 v$.	p_H.	$10^5 v$.	p_H.	$10^5 v$.	p_H.	$10^5 v$.
—	—	—	—	4·62	3·02	4·67	3·41
4·85	2·70	—	—	4·54	2·74	4·57	3·02
4·48	2·38	—	—	4·45	2·49	4·50	2·70
4·39	2·17	4·46	2·40	4·40	2·32	4·43	2·58
4·31	2·01	4·35	2·18	4·35	2·25	4·37	2·43
4·24	1·96	4·26	2·07	4·29	2·21	4·31	2·40
4·17	1·97	4·18	2·08	4·25	2·18	4·26	3·37
4·12	1·98	4·11	2·09	4·19	2·19	4·22	3·38
4·00	2·10	4·00	2·30	4·12	2·20	4·16	2·40
3·92	2·36	3·87	2·70	4·05	2·33	4·09	2·49
3·79	2·70	3·70	3·50	3·96	2·54	4·02	2·64
3·73	3·13	—	—	3·85	2·85	3·95	2·82
3·63	3·71	—	—	3·79	3·17	3·86	3·12
—	—	—	—	3·74	3·40	3·79	3·51

It will be seen from the figure that as c increases, the minimal velocity increases and becomes displaced towards regions of lower hydrion concentration, as might have been expected on the basis of equations (4) and (5).

From these curves the v–c curves can readily be plotted. They are shown in Fig. 3 for each 0·1 unit of p_H from p_H 4·6 to p_H 3·8 inclusive, the numerals showing the p_H value to which each point corresponds. When points relating to the same p_H are joined, straight lines are obtained which, on production to the axis of velocities, yield the velocity data which should pertain to the salt-free solution.

The data obtained from the intercepts on the axis of velocities are shown in connexion with the lowest (broken) curve of Fig. 2. They are compared in Table VI with the requirements of equation (16), in which the values used are $h_0 = 6·76 \times 10^{-5}$, $u_0 = 1·76 \times 10^{-5}$, and $w_0 = 0·06 \times 10^{-5}$.

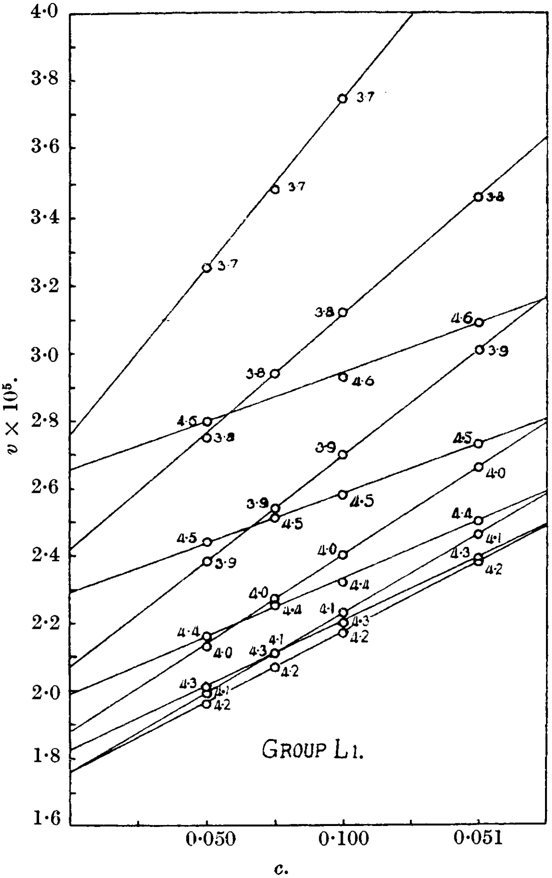
TABLE VI.

p_H	4·6	4·5	4·4	4·3	4·2
$10^5 v_0$	2·66	2·29	1·99	1·82	1·76
$10^5 v_0$ (calc.)	2·67	2·27	1·99	1·83	1·76
Diff.	−0·01	+0·02	±0·00	−0·01	±0·00

p_H	4·1	4·0	3·9	3·8
$10^5 v_0$	1·76	1·89	2·09	2·42
$10^5 v_0$ (calc.)	1·78	1·89	2·08	2·43
Diff.	−0·02	±0·00	+0·01	−0·01

It is noteworthy that the slopes of the v–c curves are approximately constant at p_H's above 4·3, but on the acid side of this value they increase more and more rapidly as the p_H decreases. It is possible from the limiting slope and the divergences of slope, to make rough estimates of k_a and k_m respectively, although, of course, the experiments were not designed with the object of measuring those quantities, and are not of the most suitable kind for that purpose. It appears, however, that k_a and k_m are both of the order of a few units times 10^{-5}.

FIG. 3.



(E) *Short Summary of Results*.—The v–p_H data (10^5v) for the esters and salt concentrations employed, obtained as illustrated in Sections C and D, are collected in Table VII. The extrapolated

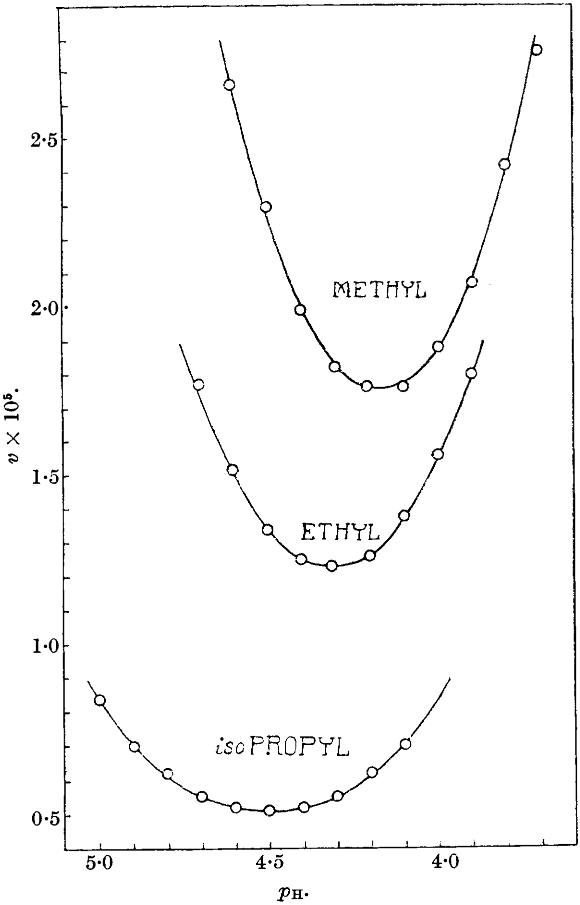
TABLE VII.

100 *c*.	5	7·5	10	15	5	7·5	10	15	5	7·5	10	15	5	7·5	10	15
Ester.	Methyl.				Ethyl.				*n*-Propyl.				*iso*Propyl.			
p_H.																
5·0	—	—	—	—	—	—	—	—	—	—	—	—	0·89	—	0·95	1·00
4·9	—	—	—	—	—	—	—	2·67	—	—	—	2·45	0·76	—	0·82	0·87
4·8	—	—	—	—	—	—	2·20	2·26	—	—	2·05	2·11	0·66	—	0·72	0·76
4·7	—	—	—	3·58	1·83	—	1·90	1·96	1·70	—	1·77	1·83	0·60	—	0·65	0·70
4·6	2·80	—	2·93	3·09	1·59	—	1·66	1·74	1·49	—	1·56	1·63	0·57	—	0·62	0·67
4·5	2·44	2·51	2·58	2·73	1·43	—	1·51	1·60	1·35	—	1·44	1·52	0·56	—	0·61	0·67
4·4	2·16	2·25	2·32	2·50	1·35	—	1·46	1·55	1·29	—	1·40	1·50	0·58	—	0·63	0·69
4·3	2·01	2·11	2·20	2·39	1·34	—	1·45	1·56	1·30	—	1·42	1·53	0·62	—	0·68	0·75
4·2	1·96	2·07	2·17	2·38	1·39	—	1·52	1·65	1·38	—	1·51	1·65	0·69	—	0·76	0·84
4·1	1·99	2·11	2·23	2·46	1·53	—	1·68	1·83	1·54	—	1·69	1·85	0·78	—	0·87	—
4·0	2·13	2·27	2·40	2·66	1·83	—	1·90	2·06	1·76	—	1·93	2·12	0·90	—	—	—
3·9	2·38	2·54	2·70	3·01	2·00	—	2·20	2·40	2·04	—	2·26	2·48	—	—	—	—
3·8	2·75	2·94	3·12	3·46	2·39	—	—	—	—	—	—	—	—	—	—	—
3·7	3·26	3·50	3·74	—	—	—	—	—	—	—	—	—	—	—	—	—
Ester.	*n*-Butyl.				*iso*Butyl.				*n*-Amyl.				*iso*Amyl.			
p_H.																
4·9	—	—	—	—	—	—	2·03	2·11	—	—	—	—	—	—	—	2·21
4·8	1·88	—	1·96	2·04	1·64	1·68	1·72	1·79	1·82	1·86	1·90	1·96	1·72	1·76	1·80	1·88
4·7	1·84	—	1·72	1·80	1·42	1·46	1·50	1·57	1·57	1·62	1·66	1·73	1·49	1·54	1·58	1·65
4·6	1·45	—	1·53	1·62	1·25	1·30	1·34	1·42	1·39	1·43	1·48	1·56	1·32	1·36	1·41	1·49
4·5	1·31	—	1·41	1·50	1·16	1·21	1·26	1·35	1·27	1·32	1·36	1·46	1·21	1·26	1·31	1·40
4·4	1·26	—	1·37	1·46	1·13	1·18	1·24	1·34	1·22	1·28	1·34	1·43	1·17	1·23	1·28	1·38
4·3	1·27	—	1·39	1·49	1·15	1·20	1·27	1·38	1·24	1·30	1·37	1·48	1·18	1·24	1·32	1·41
4·2	1·34	—	1·48	1·61	1·24	1·30	1·36	1·50	1·33	1·40	1·47	1·60	1·26	1·33	1·38	1·52
4·1	1·50	—	1·63	1·78	1·38	1·46	1·53	1·69	1·49	1·56	1·63	1·78	1·40	1·47	1·54	1·68
4·0	1·69	—	1·85	2·01	1·57	1·66	1·76	1·94	1·68	1·76	1·85	2·02	1·59	1·68	1·75	1·92
3·9	1·97	—	2·15	2·32	1·87	—	—	—	1·96	—	2·06	—	1·84	1·94	2·03	—
3·8	2·34	—	—	—	—	—	—	—	—	—	—	—	2·26	—	—	—

velocity values ($10^5 v_0$) for buffer-free solution are in Table VIII, and are shown graphically in Figs. 4 and 5.

The curves shown in conjunction with the v–p_H data in Figs. 4 and 5 are graphs of equation (16) corresponding with certain assumed values of u_0, h_0, and w_0. The assumed values of w_0 are relatively very small (of the order 10^{-7}) and the curves are not sensitive to their absolute magnitudes; conversely, the data shown in connexion with the curves do not enable the values of w_0 to be fixed with any approach to precision. They do show, however, that the catalytic influence measured by w_0, *viz.*, that of water molecules, is only of minor importance in the hydrolysis of carboxylic esters. We think

FIG. 4.



that Skrabal and Zahorka's claim (*Monatsh.*, 1929, **53**, **54**, 562) to have shown that 36% of the minimal velocity of hydrolysis of ethyl acetate at 25° is due to water catalysis is vitiated by the omission to make allowance for buffer effects; probably the major portion of the percentage mentioned is to be laid to the account of the constituents of the buffers employed.

FIG. 5.

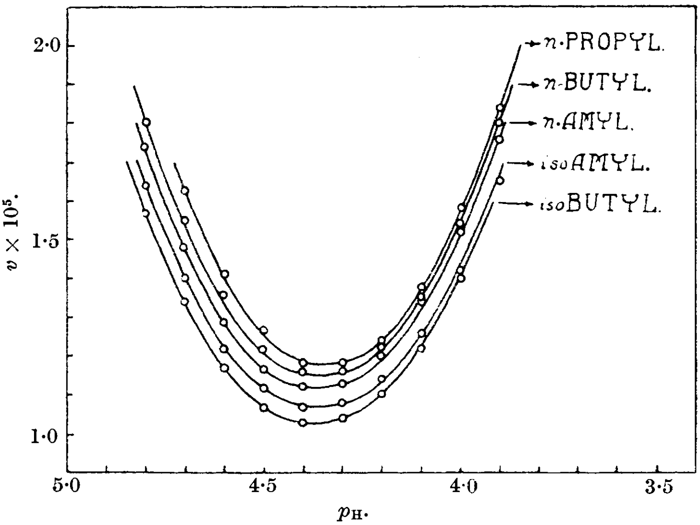


TABLE VIII.

p_H .... Ester.	5·0	4·9	4·8	4·7	4·6	4·5	4·4
Methyl	—	—	—	—	2·66	2·29	1·99
Ethyl	—	—	—	1·77	1·52	1·34	1·25
n-Propyl	—	—	—	1·64	1·42	1·27	1·18
*iso*Propyl	0·84	0·70	0·62	0·55	0·52	0·51	0·52
n-Butyl	—	—	1·80	1·55	1·36	1·22	1·16
*iso*Butyl	—	—	1·57	1·34	1·17	1·07	1·03
n-Amyl	—	—	1·74	1·48	1·29	1·17	1·12
*iso*Amyl	—	—	1·64	1·40	1·22	1·12	1·07

p_H .... Ester.	4·3	4·2	4·1	4·0	3·9	3·8	3·7
Methyl	1·82	1·76	1·76	1·88	2·07	2·42	2·77
Ethyl	1·23	1·26	1·38	1·56	1·80	—	—
n-Propyl	1·18	1·24	1·38	1·58	1·82	—	—
*iso*Propyl	0·55	0·62	0·70	—	—	—	—
n-Butyl	1·16	1·22	1·35	1·53	1·80	—	—
*iso*Butyl	1·04	1·10	1·22	1·40	—	—	—
n-Amyl	1·13	1·20	1·34	1·51	1·76	—	—
*iso*Amyl	1·08	1·14	1·25	1·43	1·65	—	—

The values u_0 and h_0 correspond with the co-ordinates of the minima of the curves. They are given in Table IX, together with the corresponding values of $p_{\mathrm{H}}{}^* = -\log_{10}h_0$, and of $k_{\mathrm{OH}}/k_{\mathrm{H}} = h_0{}^2/K_w$. In the calculation of $k_{\mathrm{OH}}/k_{\mathrm{H}}$ it is necessary to assume a figure for K_w, and $10^{1 \cdot 23-14}$ has been adopted as the result of interpolation from existing data. The value is inevitably arbitrary for the reason mentioned on p. 1045, but, as is there explained, there is reason to believe that its arbitrariness will not affect the purpose for which these measurements have been made.

TABLE IX.

Ester.	$u_0 \times 10^6$.	$h_0 \times 10^6$.	$p_{\mathrm{H}}{}^*$.	$(k_{\mathrm{OH}}/k_{\mathrm{H}}) \times 10^{-3}$.
Methyl *dl*-glycerate	17·6	68·4	4·165	27·5
Ethyl ,, ...	12·3	47·9	4·320	13·5
n-Propyl ,, ...	11·8	44·7	4·350	11·8
*iso*Propyl ,, ...	5·1	31·3	4·505	5·8
n-Butyl ,, ...	11·5	44·2	4·355	11·5
*iso*Butyl ,, ...	10·3	42·7	4·370	10·7
n-Amyl ,, ...	11·2	43·7	4·360	11·2
*iso*Amyl ,, ...	10·7	43·7	4·360	11·2

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[*Received, March 5th,* 1930.]