those by the scavenger technique[10] but were much less precise. Strong and Willard[8] have improved on the accuracy by using an analog computer, and the advantages of getting both quantities from a single type of measurement are obvious. However, from its very nature flash photolysis can scarcely employ really monochromatic light, and scavenger techniques will continue to be preferred for measuring accurate quantum yields especially as a function of wave length.

Acknowledgment.—This research was supported in part by the U. S. Atomic Energy Commission under Contract AT(30-1)-1314.

The authors are indebted to Professor George Porter of the University of Sheffield for pointing out that changes in viscosities of solvents are usually greater than changes in diffusion coefficients of a specific solute in these solvents.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rate Studies on Complex Reaction Systems in a Stirred Flow Reactor: The Alkaline Hydrolysis of Diethyl Succinate[1]

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The applicability of the continuous flow stirred tank reactor to kinetic studies of complex reaction systems has been demonstrated for the two-step alkaline hydrolysis of diethyl succinate in 70% ethanol. The method is exact but loses some of its success, as do other kinetic procedures, when applied to reactions involving medium effects. The data obtained show that k_1, the specific rate for the first saponification step, is subject to a primary salt effect which is specific to the succinate ion formed during the reaction. The rate is depressed with increasing succinate ion concentration, the magnitude of the depression at the same time depending upon the sodium ion concentration in the reaction medium. The specific rate for the second saponification step, k_2, exhibits a positive salt effect with increasing sodium ion concentration. The salt effects are not determined by ionic strength. The differences in rate between the first and second steps appear to be wholly accounted for by differences in activation entropy, with the activation energy for the second step actually lower than that for the first. An improvement in experimental technique has been described whereby the reaction vessel is internally rather than externally thermostated. Actual reaction temperatures are, therefore, not influenced by differences in heats of reaction brought about by differences in concentrations of reactants. It has also been shown that pumping devices employing pulsating flows may be used without adverse effect upon approach to and attainment of steady-state conditions.

The theory of the continuously flowing stirred tank reactor has been discussed previously by Denbigh[2] and by Hammett.[3] When applied to the study of non-integrable complex reaction systems, this technique offers an exact method for evaluation of specific rates, since rate equations are immediately expressible in algebraic rather than differential form. We have applied the technique to the saponification of diethyl succinate, a symmetrical diester in a solvent medium of 70% ethanol. This system, an example of a pair of competitive, consecutive second-order reactions, may be represented by the equations

$$A + B \xrightarrow{k_1} C + E$$

$$B + C \xrightarrow{k_2} D + E$$

A represents the diester, B the hydroxide ion and C the half-saponified or monoester.

Ingold,[4] Ritchie,[5] and Westheimer, Jones and Lad[6] were successful in determining values of k_1 in such reaction systems by independent measurement of k_2 on the monoester combined with approximate methods of integration in experiments involving the complete system. Frost and Schwemer[7] have presented a "time-ratio" method of numerical analysis which permits evaluation of both rate constants from the data of a single run. The method, however, suffers from the disadvantage that the initial concentrations must be stoichiometrically equivalent. Wideqvist[8] has extended the usefulness of this method to all ratios of initial concentrations but relies upon a graphical integration for evaluation of the new parameter introduced.

Symbols.—These symbols are used in this paper

a_0, b_0	concn. of reactants in the entering liquid
a_s, b_s, c_s	concn. of reactants in the reactor at steady state
a', b', c'	concn. of reactants at point of quenching
u	total flow rate
V	reactor volume
V^1	volume of exit tube
w	reduced flow rate $= u/V$
r_1, r_2	instantaneous rates of first and second reaction steps
k_1, k_2	second-order specific rates of first and second reaction steps

Method of Evaluation of Specific Rates.—The flow equations for each reactant in the steady state are

$$w(a_0 - a_s) - r_1 = 0 \tag{1}$$

$$w(b_0 - b_s) - r_1 - r_2 = 0 \tag{2}$$

$$-wc_s + r_1 - r_2 = 0 \tag{3}$$

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[1] Based on a dissertation submitted by Robert L. Burnett in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] K. G. Denbigh, *Trans. Faraday Soc.*, **40**, 352 (1944); **44**, 479 (1948).

[3] H. H. Young and L. P. Hammett, THIS JOURNAL, **72**, 280 (1950); J. Saldick and L. P. Hammett, *ibid.*, **72**, 283 (1950); M. J. Rand and L. P. Hammett, *ibid.*, **72**, 287 (1950).

[4] C. K. Ingold, *J. Chem. Soc.*, 2170 (1931).

[5] M. Ritchie, *ibid.*, 3112 (1931).

[6] F. H. Westheimer, W. A. Jones and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942).

[7] A. A. Frost and W. C. Schwemer, THIS JOURNAL, **73**, 4541 (1951); **74**, 1268 (1952).

[8] S. Wideqvist, *Arkiv Kemi*, **8**, 325 (1955). See also W. G. McMillan, THIS JOURNAL, **79**, 4838 (1957).

Since k_1 and k_2 are, by definition, specific rates, an assumption that these quantities are independent of medium effects is not necessarily made when one substitutes into the above equations, $r_1 = k_1 a_s b_s$ and $r_2 = k_2 b_s c_s$. With these substitutions, equations 1, 2 and 3 may be combined to give

$$k_1 = \frac{w(b_0 - b_s)(w + k_2 b_s)}{w b_s(a_0 - b_0 + b_s) + k_2 b^2_s(2a_0 - b_0 + b_s)} \quad (4)$$

If the steady-state concentration of hydroxyl ion is measured in each of two experiments which differ in the values of flow rate or input concentrations, one may obtain from equation 4 two equations which may be solved simultaneously for k_1 and k_2, provided that k_1 and k_2 are independent of medium effects. This assumption of constancy may be tested by the consistency of the data of three or more experiments. In the present work, tests for consistency led to values of k_1 which varied over a range of 20% or more and values of k_2 which varied as much as 100%. One pair of flow runs, in fact, did not yield a real solution by the above method.

Since medium effects were indicated by these inconformities, an investigation of k_2 as a function of concentration was undertaken separately by conventional batch measurements on the monoester. With such prior knowledge of k_2, it is possible to solve equation 4 for a value of k_1 which is unambiguously the specific rate for the particular reaction medium in which the measurements were made.

Experimental

Apparatus.—A schematic representation of the apparatus is given in Fig. 1. Constant rate of delivery of diethyl succinate to the reactor in the flow measurements was achieved with a motor-driven syringe operating through a gear reduction box.[9] Base flow was controlled by means of a commercially available positive displacement diaphragm pump employing only stainless steel and Kel-F plastic liquid-handling parts (Lapp Microflow Pulsafeeder, Model LS-10, Lapp Insulator Co., Le Roy, New York). Alcoholic base solution was fed by gravity from a five-gallon polyethylene reservoir protected by Ascarite tubes into the inlet side of the pump and flow rates obtained were continuously variable. Since the flow furnished by the pump was of a pulsating nature, a small vertical air pocket was placed in the tubing between pump and reactor to eliminate most of the irregularity of flow from this cause. Experiments proved, however, that due to the fairly rapid frequency of pulsation (45 strokes/min.), runs involving total flow rates up to at least 10 ml./min. could be accommodated with or without pulsation suppressed in this way with no effect upon the calculated specific rates.

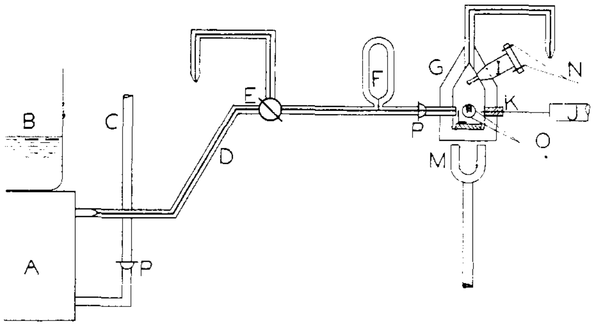

Fig. 1.—Schematic diagram of flow apparatus: A, Pulsafeeder pump; B, reagent reservoir for alcoholic base; C, syphon tube from reservoir to inlet side of pump; D, 1 mm. capillary tubing from outlet side of pump to flow reactor; E, stopcock for bypass tube; F, vacuum-jacketed air pocket for pulse elimination; G, flow reactor; H, platinum coil heater; I, thermistor assembly; J, ester syringe; K, syringe needle entering reactor through rubber stopper; L, stirring bar; M, stirring magnet; N, thermistor leads to Thermonitor temperature regulator; O, heater leads from Thermonitor; P, ground glass ball joints.

A departure from previous methods[3,9] was employed in the reactor construction and temperature control. The temperature of the reaction mixture was regulated internally rather than externally by means of a thermistor and platinum heater in direct contact with the liquid. Use was made of a commercial temperature detecting and regulating device (Sargent Thermonitor, Model S, E. H. Sargent and Co., Chicago, Illinois) which provided heat to the reaction vessel proportional to the degree of imbalance from the desired temperature setting. The reactor was vacuum-jacketed for insulation but was not silvered in order to permit vision into the vessel. The volume of the reactor, exclusive of overflow tube was determined to be 48.29 ± 0.04 ml. at 40°. It was found that flows up to 12 ml./min. at 30°, 10 ml./min. at 40° and 8 ml./min. at 50°, with reservoir temperatures at 25–28°, could be accommodated with temperature control maintained at ±0.05° or better. Since the extent of temperature variation during a run could not be determined from observation of the Thermonitor unit alone, it was necessary to tap the circuit of the instrument after the first state of output amplification and to measure the voltage between this point and ground with a high impedance vacuum tube voltmeter. The voltage fluctuation was found by measurements involving a second regulating instrument, to be proportional to the degree of imbalance in the circuit in the close vicinity of the regulating temperature. The platinum coil heater was constructed from a length of 0.005 inch diameter wire of 4.3 ohms resistance. It was necessary to place a resistance of approximately 44 ohms in series with this heater and external to the cell in order to satisfy the requirements of the Thermonitor circuit for a 250-watt capacity regulating heater.

Employment of this method of temperature control offers the advantages that reaction temperatures may be accurately reproduced regardless of variations in heats of reaction and that the apparatus need not be immersed in a large constant temperature bath.

Batch measurements on the specific rate of the monoester hydrolysis were made in a simple apparatus consisting of a thermostated volumetric flask protected from absorption of carbon dioxide by a flow of prepurified nitrogen.

Materials.—Selection of materials, standardization of solutions for titration and calibration of temperature equipment, analytical weights and volumetric glassware met customary standards for precision work. Diethyl succinate (Eastman Kodak Co.) was dried over anhydrous magnesium sulfate and distilled twice through a 25-cm. vacuum-jacketed Vigreux column under 17 mm. pressure. Saponification value was 100.0%, and the index of refraction, n^{20}D, was 1.4199. Ethyl hydrogen succinate was prepared from succinic anhydride and ethyl alcohol in a manner analogous to the preparation of methyl hydrogen succinate.[10] The product was purified in the same manner as for the diester, the distillation being carried out at approximately 0.2 mm. pressure. Since the monester exhibited a readiness during preparation and purification to disproportionate to succinic acid and the diethyl ester, the distillation equipment was steamed before use to remove traces of acid or base; and the distillation was carried out at as low a temperature as possible. Neutral equivalent determinations on the monoester resulted in a molecular weight of 145.2 compared with the theoretical 146.1. The refractive index, n^{20}D, was 1.4327. Seventy per cent. ethanol compositions were prepared in 15-liter batches by dilution with water of 95% ethanol which had been distilled through a one meter column packed with $^3/_{32}$ inch glass helices at a reflux ratio of 15:1. Percentage compositions were checked by density measurement.

Method.—In making a flow run, the reactor was initially filled with alcoholic base solution with the pump running at

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(9) H. M. Humphries and L. P. Hammett, THIS JOURNAL, **78**, 521 (1956).

(10) E. C. Hornung, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 169.

the desired speed. After the reactor was filled, the pump flow was diverted by means of the by-pass stopcock (see Fig. 1), and the ester flow was started. When the ester flow had proceeded for a time corresponding to one volume turnover at the total flow rate chosen, the base flow was again directed into the cell and the run begun. During the approach to the steady state, timed overflow samples were collected and weighed to determine the total flow rate. An additional sample was collected for this purpose after quenching of the analytical samples in order to ensure that no change in pumping rate had occurred. A knowledge of the ester flow rates, which were constant to ±0.1–0.2%, and the density of the base solution in the pumping reservoir was sufficient for calculation of the base flow and total flow rates. Pumping rates were found constant to ±0.1% or better. After passage of at least seven volumes of reaction mixture through the cell,[3] three timed samples of approximately one cell volume each were quenched in pipetted quantities of acetic acid solution and saved for analysis by back-titration with sodium hydroxide using phenolphthalein as indicator. Carbon dioxide was excluded during these titrations with a flow of prepurified nitrogen.

Adequate stirring of the reactor was achieved at a rate of 300–400 r.p.m. of the magnetic stirring bar. The presence of the platinum heater in the reactor was an aid in producing a more turbulent stirring action.

It was necessary to apply to the measured hydroxide ion concentration a correction for the amount of reaction occurring in the overflow tube before quenching. The method of Saldick and Hammett[3] is not applicable here, since the reaction is of a complex nature. The differential equations representing the change in concentrations of the reacting species when in the exit tube may be written as

$$\mathrm{d}a/\mathrm{d}t = -\,k_1ab \qquad (5)$$

$$\mathrm{d}b/\mathrm{d}t = -\,k_1ab - k_2bc \qquad (6)$$

$$\mathrm{d}c/\mathrm{d}t = k_1ab - k_2bc \qquad (7)$$

When $t = 0$, the volume element of reaction mixture under consideration has not yet entered the exit tube, and all concentrations are those of the steady state. When $t = V'/u$, the volume element of reaction mixture is quenched and analyzed. The concentrations at this point are a', b' and c'. The above differential equations may be integrated by a power series expansion to give, after imposition of the boundary conditions stated, the expression

$$b_s = b' + (k_1a'b' + k_2b'c')(V'/u) + \ldots \qquad (8)$$

b' is determined experimentally, but a' and c' are not. However, a value of k_1 may be calculated from a knowledge of k_2 and the experimental quantities using equation 4. Values for the corresponding a and c, if b' were the steady-state concentration, may then be calculated from equations 1 and 3 and these substituted for a' and b' in equation 8. The error introduced by using the first calculated values of a and c for a' and c' is negligible, since the magnitude of the correction is very small. Since $V' = 0.166 \pm 0.003$ ml., the first two terms on the right-hand side of equation 8 are sufficient for the calculation of b_s. The value of b_s is then used to calculate a better value of k_1, one such cycle of calculations being adequate to account for the small amount of reaction taking place in the exit tube. The correction applied usually resulted in a difference in k_1 of approximately 1–2%.

The batch measurements were carried out by conventional procedures of removal and quenching of reaction samples during the course of a reaction. Values of k_2 were calculated from second-order plots of the data by the method of least squares.

Results and Conclusions

Batch Measurements.—Information on the dependence of k_2 upon concentration was obtained at 30, 40 and 50° in order that interpolated values of k_2 could be used for the calculation of k_1 from equation 4.

The value of k_2 was determined to be a function of the concentration of sodium ion present in the solution and not upon the ionic strength. Two items of evidence are offered to support this conclusion. First, application of the second-order rate equation to the experimental data resulted in reasonably constant calculated values of k_2 to very high conversions in all runs. This is shown graphically in Fig. 2, a second-order plot of a typical run involving conversion of base up to 82%. During the course of this reaction, the ionic strength increased approximately 25% due to the formation of succinate ion. The second evidence was obtained by addition of succinate ion to a reaction mixture to increase the ionic strength. This was accomplished without change in the sodium ion concentration by addition of succinate in the form of succinic acid. The calculated specific rate agreed within experimental error (± 1.0–1.5%) with that obtained for reaction mixtures of approximately equal sodium ion concentration but without added succinate. A summary of data at 40° appears in Table I. Figure 3 shows the variation of k_2 with sodium ion concentration at the three temperatures. The estimated precision of the values of k_2 interpolated from these curves for use in the calculation of k_1 was ± 1.5%.

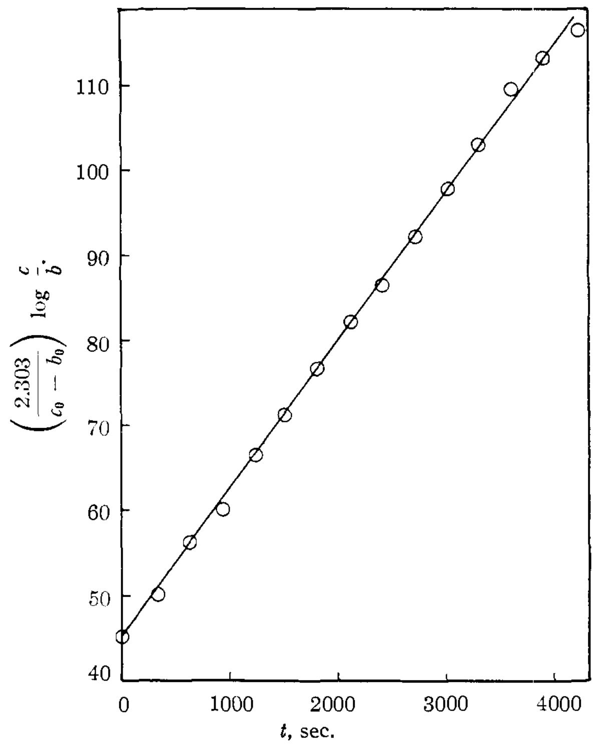

Fig. 2.—Second-order plot of alkaline hydrolysis of monoethyl succinate ion in 70% ethanol at 40°.

TABLE I

RATE DATA ON SECOND SAPONIFICATION AT 40°

(Concentrations in mole/l.)

k_2 (l. mole $^{-1}$ sec. $^{-1}$)	Total Na$^+$ ion concn.	Mean ionic strength	Concn. NaCl added	Concn. succinate ion added
0.0175	0.0475	0.0578	....	.....
.0178	.0477	.0578	....	.....
.0176	.0476	.0566	....	.....
.0177	.0482	.0641	....	0.00854
.0205	.0706	.0838	0.0224	.....
.0214	.0814	.0947	.0332	.....
.0237	.1154	.1575	....	.....

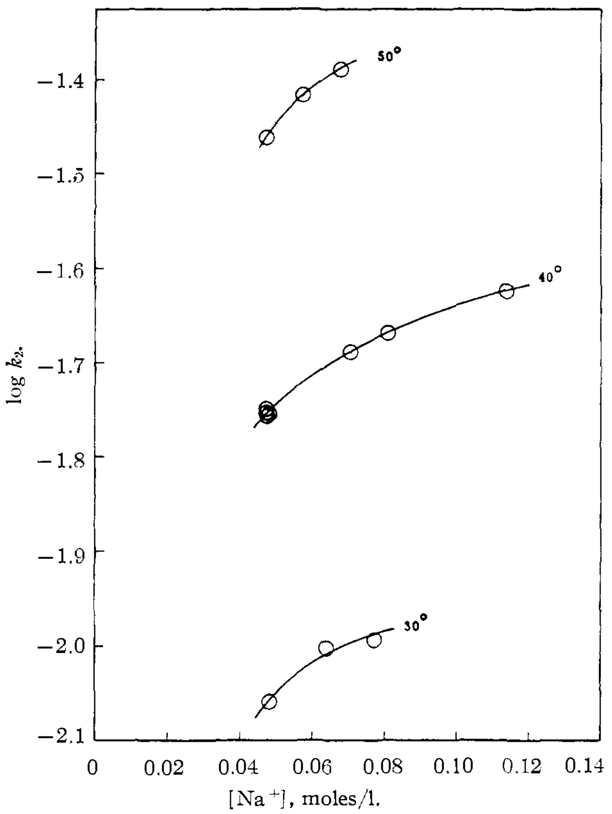

Fig. 3.—Dependence of k_2, the specific rate of alkaline hydrolysis of monoethyl succinate ion, upon sodium ion concentration in 70% ethanol at 30, 40 and 50°.

The observed dependence of k_2 upon sodium ion concentration is in agreement with the evidence presented by Olson and Simonson[11] that for reactions between ions of the same charge sign, the effect of the addition of "inert" salts is determined almost exclusively by the concentration and character of the added ions of charge opposite to that of the reactants. They found that the rates of such reactions were not dependent upon the ionic strength of the solution.

Westheimer, Jones and Lad[6] reported a salt effect on k_2 for the saponification of the half-esters of malonic and adipic acids which was dependent upon ionic strength over a range from 0.0065 to 0.096 *M*. They obtained values for k_2^0, the specific rate at infinite dilution, by extrapolation with an equation derived from the Brønsted activity rate equation

$$k_2 = k_2^0 \frac{f_B f_C}{f_X} \qquad (9)$$

and a form of the Debye–Hückel limiting law

$$\log f = -\alpha Z^2 \sqrt{\mu} + B\mu$$

In the above equations f_B f_C, and f_X represent the activity coefficients of reactants and activated complex, respectively; μ is the ionic strength; Z is the ionic charge; and α and B are constants. It is not possible from the data of the above investigators to ascertain whether a better correlation could be drawn between specific rate and sodium ion concentration. Tommila and Kivinen[12] have likewise reported a salt effect dependent upon ionic strength for the saponification of the monoethyl esters of acetylene dicarboxylic acid and succinic acid at concentrations of 0.01 *M* and less. These workers also made use of a Debye–Hückel plot in determining limiting values of k_2. Data given by them for a sample run, however, fail to reveal an increase in the second-order specific rate calculated at various reaction times corresponding to an over-all increase in ionic strength of 30%. Ingold[3] and Ritchie[4] made no mention of salt effects in their studies of saponification rates for various dicarboxylic monoesters.

There appears to be little doubt as to the general validity of the Brønsted equation (equation 9). However, application of the Debye–Hückel limiting law for estimation of the activity coefficient term often leads to serious difficulties in any but the most dilute of solutions, since specific interactions between ions in solution apparently influence the values of the activity coefficients. In the case of the saponification of diethyl succinate, the magnitude of the quantity $f_B f_C / f_X$ increases with sodium ion concentration; but in the absence of a satisfactory theory, no attempt at extrapolation to infinite dilution was made in the present work.

Flow Measurements.—Experimental proof of the lack of effect of pulsation of the basic flow upon the approach to the steady state was obtained in two sets of runs at 40° by determining the steady-state concentration of base under identical conditions of flow rate and input concentrations. One run in each set was made with a maximum degree of pulsation and the other runs with the pulsation suppressed as far as possible. Specific rates observed in each case were identical within the limits of experimental error, as summarized in Table II.

Table II

Effect of Pulsation

(Concentrations in moles/l., k_1 in l./mole sec.)

Pulse removed	u (ml./min.)	a_0	b_0	b_S	d_S	k_1, %
Yes	10.025	0.04757	0.04739	0.02496	0.00227	0.1020 ± 1.7
Yes	10.047	.04738	.04739	.02496	.00227	.1029 ± 1.3
No	10.146	.04689	.4740	.02512	.00225	.1041 ± 1.4
Yes	10.107	.06857	.04722	.01974	.00228	.1027 ± 1.2
No	10.071	.06870	.04722	.01974	.00229	.1019 ± 1.2

Detailed information for the dependence of k_1 on concentration was obtained at 40° and sufficient data obtained at 30 and 50° to provide for calculation of the variation of rate with temperature. Experiments revealed a dependence of rate upon concentration of succinate ion present in the steady state. Calculated specific rates decreased in value with increasing succinate concentration, the magnitude of the depression of rate being greater the smaller the total sodium ion concentration. The experimental data at 40° are summarized in Table III. Values of the succinate ion concentration were calculated from equations 1 and 3 and from mass balance relations. The uncertainties in k_1 were calculated by partial differentiation of equation 4

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[11] A. R. Olson and T. R. Simonson, *J. Chem. Phys.*, **17**, 1167 (1949).

[12] E. Tommila and A. Kivinen, *Suomen Kemistilehti*, **27B**, 1-A (1954).

with respect to each of the measurable quantities and insertion of appropriate estimates of the errors in these quantities into the differential expressions. The data of Table III are plotted in Fig. 4. The apparent near-linear dependence upon the succinate ion concentration of k_1 at each of the three sodium ion concentrations suggested plotting the data in the manner shown. The locations of the straight lines were determined by a weighted method of least squares. Calculated intercept values of k_1 at zero succinate ion concentration were 0.1214 ± 0.0034, 0.1164 ± 0.0055 and 0.1129 ± 0.0023. This suggests that the limiting values of k_1 may be identical, at least for the two lower sodium ion concentrations. Four runs each at 30 and 50° in solutions approximately 0.0475 *M* in sodium ion provided data for calculation of the temperature dependence of k_1. An additional run at 30° in 0.0710 *M* sodium ion resulted in behavior analogous to that at 40°: an increase in rate above that accountable for by experimental error was observed.

TABLE III

RATE DATA ON FIRST SAPONIFICATION AT 40°

(Concentrations in moles/l., k_1 in l./mole sec.)

k_1	Uncertainty in k_1, %	Na$^+$ ion concn.	Succinate ion concn.
0.1041	1.4	0.0474	0.0022
.1029	1.3	.0474	.0023
.1027	1.2	.0472	.0023
.1020	1.7	.0474	.0023
.1019	1.3	.0472	.0023
.0975	1.8	.0476	.0034
.0956	1.4	.0474	.0039
.1053	3.3	.0712	.0048
.1044	2.0	.0710	.0057
.1023	1.8	.0708	.0067
.0986	1.2	.0707	.0083
.1196	3.4	.1157	.0088
.1191	2.6	.1156	.0092
.1147	2.2	.1154	.0107
.1203	2.5	.1154	.0110
.1125	1.2	.1141	.0128
.1129	1.2	.1125	.0166
.1121	1.9	.1148	.0192

Since the presence of the doubly charged succinate ion appears to decrease the rate in the first saponification step, the question arose as to whether other doubly charged negative ions might produce similar effects. An extensive investigation to this end was not undertaken, but one experiment involving a solution approximately 0.0142 *M* in sulfate ion at a sodium ion concentration of approximately 0.0475 *M* resulted in a calculated value of 0.093 for k_1 at 40°.

The alkaline hydrolyses of esters of monocarboxylic acids at moderate concentrations are generally regarded as being uninfluenced or very slightly influenced by salt effects.[13] The evidence for this conclusion is not in disagreement with the results of the present work, since there appears to be little, if any, effect of total ion concentration on specific rate in the absence of succinate ion. The possibility suggests itself that similar salt effects of doubly charged negative ions are present in the saponification of esters such as ethyl acetate. No evidence of any experiments along this line was found in the literature, and it remains a matter of interest as to the behavior under these conditions.

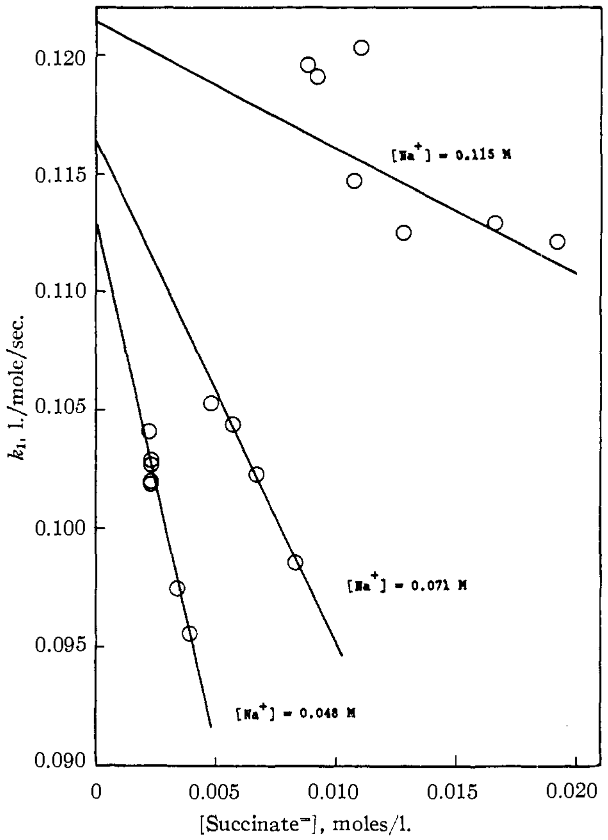

Fig. 4.—Dependence of k_1, the specific rate of the first step in the alkaline hydrolysis of diethyl succinate, upon succinate ion concentration in 70% ethanol at 40°.

Westheimer, Jones and Lad[6] have reported the first saponification constants for diethyl malonate and diethyl adipate to be nearly uninfluenced by salt concentration. Ritchie,[5] Ingold,[4] and Tommila and Kivinen[12] have made no mention of salt effects on k_1 for various dicarboxylic esters; and Frost and Schwemer[7] carried out measurements in a medium 0.02 *M* in KCl, which undoubtedly swamped out effects of this kind. It appears that previous methods employed in studying the kinetics of alkaline hydrolysis of dicarboxylic esters have not provided sufficient precision to establish the existence of medium effects on the first specific rate. The flow method provides proof of variations of this kind: the over-all experimental variation in calculated specific rates at 40° was more than 20%, while the precision of any one determination ranged from 1.2–3.4%.

Consider again the Brønsted equation, now written as

$$k_1 = k_1^0 \frac{f_A f_B}{f_X} \tag{9a}$$

with f_A the activity coefficient of uncharged diester and f_B and f_X the activity coefficients of charged base and activated complex, respectively. It is reasonable to expect f_B and f_X to be more nearly equal to one another in magnitude than to f_A;

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(13) S. Arrhenius, *Z. physik. Chem.*, **1**, 111 (1887).

TABLE IV

TEMPERATURE DATA FOR SAPONIFICATION OF DIETHYL SUCCINATE AT [Na^+] = 0.0475 *M* AND [SUCCINATE$^=$] = 0.0030 *M*

Reaction	k, l./mole sec. 30.00°	40.00°	50.00°	E_a (kcal.)	log A	40° $\Delta H^{\ddagger}$ (kcal.)	40° $\Delta S^{\ddagger}$ (cal./deg.)
1st step	0.0462 ± 1.5%	0.0995 ± 1.5%	0.1956 ± 1.1%	14.00 ± 0.29	8.76 ± 0.20	13.38 ± 0.29	−20.52 ± 0.91
2nd step	0.00866 ± 1.5%	0.0177 ± 1.5%	0.0346 ± 1.5%	13.54 ± 0.20	7.70 ± 0.14	12.92 ± 0.20	−25.38 ± 0.64

and it therefore appears likely that the observed effect is due to a specific "salting-in" or decrease in f_A by succinate ion. The usual application of the Debye–Hückel limiting law in its simpler forms predicts either no variation with ionic strength of the ratio $f_A f_B / f_X$, or a small linear variation, depending upon the form used.

Long, McDevit and Dunkle[14] have given some results for a reaction between a neutral molecule and an ion which may provide a helpful comparison. The reaction studied is the acid-catalyzed hydrolysis of γ-butyrolactone to γ-hydroxybutyric acid. The rate is proportional to the concentration of hydrogen ion and of lactone. They observed salt effects of varying magnitude and in opposite directions upon the hydrolysis rate. Addition of sodium chloride accelerated the reaction, while sodium perchlorate showed depression of the rate. Independent distribution experiments established that sodium chloride exhibited a "salting-out" or increase in the activity coefficient of the lactone, while sodium perchlorate caused a "salting-in" or decrease in activity coefficient. The conclusion to be drawn is that the effect on the rate of the quantity $f_{H_3O^+}/f_X$ is of relatively smaller magnitude than that of f_{lactone}.

Temperature Dependence of Specific Rates.—Temperature data for the first and second saponification steps for diethyl succinate are given in Table IV. The values for log A and E_a were obtained from Arrhenius slope-intercept plots and $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ were then calculated from theoretical relations. Errors in the above quantities were estimated from the least squares standard deviations of the appropriate plots. A comparison with saponification data for ethyl acetate, ethyl propionate and ethyl butyrate in 70% ethanol is also given in Table V. The information on these three reactions was interpolated from the data of Tommila, *et al.*[15] The data imply that all differences in rate are determined by differences in the entropies of activation. When the saponification of the monoester of succinic acid is excluded, it is seen that all other activation enthalpies appear equal within limits of experimental error. It should be noted that a statistical entropy factor of $R \ln A$ = 1.4 cal./deg. is involved in comparing the results of the first saponification of diethyl succinate with those of the other reactions. Smith and Levenson[16] and Tommila and Hietala[15b] have pointed out that the difference in rate of saponification between acetic ester and esters of higher straight chain aliphatic acids is due primarily to differences in entropy rather than in enthalpy of activation. The present data suggest, although they do not prove because of insufficient precision, that even so polar a substituent as a carboxyethyl group also affects entropy alone.

TABLE V

ALKALINE HYDROLYSIS OF ETHYL ESTERS IN 70% ETHANOL

(All data at 40°; units of k = l. mole^{-1} sec.$^{-1}$)

Ethyl ester	k	$\Delta H^{\ddagger}$ (kcal.)	$\Delta S^{\ddagger}$ (cal./deg.)
Acetate	0.0393	13.43	−22.2
Propionate	.0203	13.40	−23.6
Butyrate	.0099	13.32	−25.4

It appears probable also that the large difference in activation entropy between the two saponification steps for diethyl succinate is due primarily to a difference in the entropies of solvation. Thus, the activated complex formed by two negatively charged species has a greater binding force on solvent molecules than does a complex formed from a neutral and a negatively charged species. The more powerful solvation of the transition state in the first case would also account for the observed lowering of activation energy.

The difference in free energies of activation between the two saponification steps was used to calculate an entropy difference based upon electrostatic considerations only.[17] The value of 6.4 cal./deg. obtained is in fair agreement with the experimental non-statistical entropy difference of 3.5 cal./deg. when it is remembered that the experimental data used in the above calculations were subject to rather considerable medium effects.

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