Kinetic Salt Effect in Saponification of Ester Ions
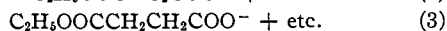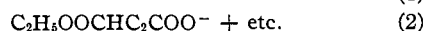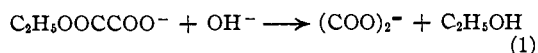
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This work was undertaken because of some apparent exceptions to the Brönsted–Debye relation between ionic strength and velocity constant of second order ionic reactions. An apparent reversal of the expected sign of the salt effect was obtained in the case of the reactions between β-bromopropionate,[1] bromomalonate, and bromosuccinate ions,[2] respectively, and thiosulfate ion. The reaction between the α-bromopropionate and thiosulfate ions, on the other hand, gives the expected sign. An explanation[1] for this was offered in terms of the position of the reacting group relative to that of the charge.

Since the experiments in this paper were begun, however, there has appeared a paper by La Mer and Greenspan[3] in which it was mentioned that the above thiosulfate reactions may be subject to complications. In this same paper, also, no difference was found in kinetic salt effect between the saponifications of α- and β-acetoxy-β-phenylpropionate ions, and the sign was that expected from Brönsted's theory. Sturtevant,[4] by a mathematical analysis, arrived at the conclusion that any such effect of the location of the reacting group relative to the charge in an ion would be negligibly small in dilute solution. The theoretical basis of the Brönsted–Debye limiting law, $\log_{10} k = k_0 + z_a z_b \sqrt{\mu}$, has also been questioned,[5] and it was suggested by La Mer and Greenspan[3] that the law may not hold quantitatively even in the limit for the reactions they studied, namely, the saponification of acetylated hydroxy ions.

It was decided to see whether there was any noticeable change in the kinetic salt effect with increasing distance of reacting group from the charge in the saponification of monoethyloxalate, monoethylmalonate, monoethylsuccinate, and monoethyladipate ions, respectively

$$C_2H_5OOCCOO^- + OH^- \longrightarrow (COO)_2^- + C_2H_5OH \quad (1)$$

$$C_2H_5OOCHC_2COO^- + etc. \quad (2)$$

$$C_2H_5OOCCH_2CH_2COO^- + etc. \quad (3)$$

$$C_2H_5OOCCH_2CH_2CH_2CH_2COO^- + etc. \quad (4)$$

It was also decided to see whether the theoretical limiting law would be fulfilled quantitatively for the reaction

$$(C_2H_5)_3N^+CH_2COOC_2H_5 + OH^- \longrightarrow$$
$$(C_2H_5)_3N^+CH_2COO^- + C_2H_5OH \quad (5)$$
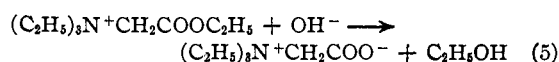
which is fast enough to have a half life (of the betaine ester) of seven minutes for a mixture beginning with the ester at 0.00005 M and the base at 0.0001 M.

Reactions (2) and (3) have been studied by Meyer,[6] but enough data were not available to determine the effect of ionic strength on the velocity constants. The same is true of reaction (1), which has been studied by Skrabal and Matievic.[7] We have followed these five reactions by a conductivity method, but only in the case of reactions (2), (3), and (4) were the conductivity data accurate enough to show the kinetic salt effect. For the relatively fast reactions (1) and (5), a photometric comparison method was used. These reactions have the disadvantage that the ionic strength changes during the course of the reactions. This error largely cancels out in comparing the various solutions, as will be discussed later.

Materials

Water.—"Conductivity" water, having a specific conductivity less than 10^{-6}, was used. No serious attempt was made to avoid carbon dioxide, since this was blown out just before each run.

Standard Sodium Hydroxide Solutions.—These were prepared, kept, and used according to accepted standards (dilution of the saturated solution with carbon dioxide-free water, paraffined containers, precautions against atmospheric air, and accepted standards and indicators).

Paraffin.—This was washed with hot, dilute sodium hydroxide, then washed repeatedly with hot water in a separatory funnel, and dried by heating above 100°.

Hydrogen.—Commercial electrolytic hydrogen was passed through an efficient train for removing any carbon dioxide present and saturated with water at the temperature of the measurements. The small amount of air in the hydrogen was of no consequence in this work.

Carbon dioxide-free air was prepared and tested in the usual way and passed through long plugs of cotton as a precaution against spray.

Potassium ethyl oxalate was prepared[8] by adding, drop by drop and with constant stirring, a solution of potassium

(1) La Mer and Kamner, THIS JOURNAL, 53, 2832 (1931).
(2) Bedford, Mason and Morrell, ibid., 56, 280 (1934).
(3) La Mer and Greenspan, ibid., 56, 1492 (1934).
(4) Sturtevant, J. Chem. Phys., 3, 295 (1935).
(5) La Mer, ibid., 1, 289 (1933).

(6) J. Meyer, Z. physik. Chem., 67, 278 (1909).
(7) Skrabal and Matievic, Monatsh., 39, 765 (1918).
(8) Freund, Ber., 17, 780 (1884).

hydroxide in absolute alcohol (about 1.5 normal) to a 10% excess of a solution (about 20%) of ethyl oxalate in absolute alcohol. About 25 g. of the ester was used for a preparation. After making sure that the solution was no longer alkaline, the product was filtered off, washed, and recrystallized from absolute alcohol and dried in a vacuum desiccator over calcium chloride. The common test for oxalate (calcium chloride in acetic acid–acetate solution) gave no precipitate.

Potassium ethyl malonate was prepared in the same way as the preceding compound except that the original mixture, after it was no longer alkaline, was heated until nearly clear and filtered, after which the crystals were allowed to settle out again. It was recrystallized and dried as above. Analysis showed 1.5 mole per cent. of normal malonate. Since this is not easily removed by recrystallization and is easily corrected for in the measurements, the product was not purified further.

Succinic Acid Monoethyl Ester.—Twenty-five grams of succinic anhydride was heated on the water-bath, under reflux and protected from atmospheric moisture, with 25 cc. of absolute alcohol, prepared with magnesium according to Lund and Bjerrum,[9] for about one and one-half to two hours until the solid anhydride disappeared. The mixture was cooled, diluted with water, and made basic with sodium carbonate. It was extracted twice with ether, made acid with hydrochloric acid, and extracted twice again. The ether layers from the acid extraction were washed, dried over calcium chloride, and heated on the steam-bath to remove the ether. The liquid was distilled under high vacuum (mercury pump) in a small round-bottomed flask, the upper portion of which was covered with carbon dioxide snow. The lower part was heated on a glycerol bath which was not allowed to go over 90°, care being taken to avoid ebullition. The distillation was stopped when about two-thirds had distilled. By keeping the residue frozen and inverting the flask, the crystalline distillate was easily removed by warming gently until it melted. It was frozen in the presence of normal hexane by a mixture of ice and salt, and the crystals were filtered quickly on a cooled "glass filter" in a stream of dry air. The product, a colorless liquid at room temperature, was dried in a vacuum desiccator over concentrated sulfuric acid containing a little chromic acid. Analysis showed absence of succinic acid within the limits of error of the titration, carried out at 0° with violent stirring.

Adipic Acid Monoethyl Ester.—This was prepared by a modification of the methods of Blaise and Koehler,[10] the one method starting with the acid and the other with the neutral ester obtained as one of the products of the first method.

First Method.—Eleven and one-half grams of adipic acid, 13 cc. of absolute alcohol, and 2.5 cc. of a normal solution of hydrogen chloride in absolute alcohol were heated together for forty-five minutes on the water-bath under reflux. The separation and extraction of the esters were the same as for the succinic compounds, except that the solution was saturated with ammonium sulfate for the acid extraction.

Second Method.—Absolute alcohol prepared as above was used throughout. A solution of 20 g. of the dried neutral ester in 25 cc. of alcohol was mixed with a solution of 2.0 g. of sodium in 50 cc. of alcohol. The resulting solution was heated to boiling and a mixture of 1.6 cc. of water and 5 cc. of alcohol dropped in over a period of about fifteen minutes. The mixture of precipitate and solution was heated for about an hour, after which most of the alcohol had evaporated. Water was added and the extractions made as before, except that the resulting basic solution made addition of sodium carbonate unnecessary.

The crude acid ester was distilled in the same way as the succinic. It was recrystallized from an ice cold mixture of ether and normal hexane by evaporating most of the ether in a stream of dry air, and filtered and dried in the same way as the succinic compound. It was, of course, necessary to keep these compounds in separate desiccators. The melting point was found to be 29° in agreement with that of Blaise and Koehler.[10]

Triethylbetaine Ethyl Ester Perchlorate.—A purified and analyzed sample of this compound was kindly furnished by Miss Kirsten Volqvartz of the institute. The salt gave the theoretical titer with sodium hydroxide in hot solution.

All the above compounds were kept in vacuum desiccators.

The Conductivity Method

Procedure.—All measurements were made at 20 ± 0.003°. The apparatus and method of measuring are those described elsewhere,[11] using hydrogen electrodes and direct current. This allows greater speed than alternating current in making readings, and the hydrogen serves as a convenient carbon dioxide-free atmosphere. The apparatus (Fig. 1) was made of orange-stripe Jena glass, but even this was not sufficiently resistant to the solutions used. Thus, the conductivity of a 0.005 N sodium hydroxide solution was found to decrease by more than 1% overnight. It was necessary, therefore, to paraffin the reservoir R and run fresh solution from the reservoir into the cell arms from time to time.

The moist, lightly platinized electrodes were put in place, and the various outlets and inlets connected to a system of stopcocks which in turn were connected to the hydrogen supply. In this way the hydrogen could be made to flow in or out at any part of the apparatus. The water or potassium chloride solution (about 300 cc.) and the ester acid or ester salt, were put into the reservoir while a stream of hydrogen flowed in at the bottom, the capillary enabling the stream of gas to keep all the liquid in the reservoir. The water, salt, and ester had, of course, been previously weighed, the latter in a stoppered weighing bottle. Hydrogen was allowed to flow through the apparatus and solution for about half an hour, so that practically all the carbon dioxide was blown out of the solution, and both the electrodes and solution saturated with hydrogen. It had been found previously that no noticeable hydrolysis takes place during this time. The base (0.3580 N) was then added through the top of the reservoir from a small weight buret filled in such a way as to avoid atmospheric carbon dioxide. In all cases enough base was added to leave an excess about equal to the original concentration of ester, after neutralization (in case of the ester acids) and saponification. The hydrogen stream

(9) Lund and Bjerrum, see C. A., **25**, 3310 (1931).

(10) Blaise and Koehler, Bull. soc. chim., [4] **7**, 218 (1910).

(11) Brönsted and Nielsen, Trans. Faraday Soc., **31**, 1478 (1935).

served both to stir the solution and to prevent entrance of air while the top of the reservoir was unplugged for inserting and removing the buret. The apparatus could be shaken to wash down any droplets that had been splashed on the upper portion of the reservoir. The time was noted to the nearest second when about half the base had run in, the total time required for addition of the base being at most about five seconds. The error due to the time required for mixing will be discussed later. It was found most convenient to use an ordinary watch that kept good time and whose second hand kept exact pace with the minute hand. Three minutes were allowed to ensure complete mixing, after which enough solution to cover the electrodes was run into the cell, the hydrogen pressure serving to drive the liquid over.
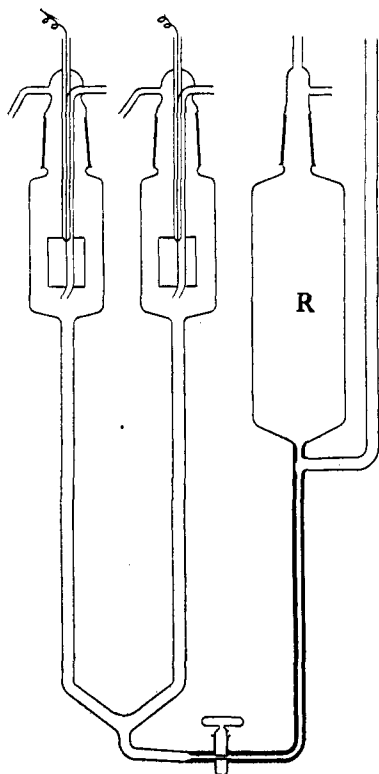

Fig. 1.

The electrodes were always found to be at the same potential as soon as the solution was in the cell. Readings were made as often as was necessary in order not to leave any doubt about any part of the time–conductivity curve and were continued until the reaction was 75–85% complete. A final reading was made when the reaction was so nearly complete that the "infinite" reading could be calculated accurately. Fresh solution was frequently run into the arms of the cell from the paraffined reservoir. As would be expected from a conductivity method, the results lay on a perfectly smooth curve.

Several possible sources of error are eliminated by the design of the cell. Since only a small part of the cell resistance is in the electrode compartments, the measured resistance corresponds almost entirely to that of the solution in the 6-mm. arms. Thus, small effects due to ad-

sorption or catalysis on the electrodes, and the use of the electrode compartments as a waste reservoir for solution that had reacted with the glass (chemically or by adsorption) were scarcely noticeable in the resistance measurements. The height of the liquid above the electrodes and the rate at which hydrogen bubbled over them did not noticeably affect the cell constant.

For the more rapid reactions (1) and (5) a modification of the above apparatus was used. This was designed to allow more rapid mixing and transference of solution from the reservoir to the cell. The U-tube joining the electrode compartments was a short 12-mm. tube since very dilute solutions were used. The base used was tenth or hundredth normal, added from a micro-buret. Since the results obtained from this apparatus were not sufficiently accurate to show the kinetic salt effect properly, the apparatus will not be described further. It served the purpose, however, of giving approximate values of the velocity constants for these reactions. The photometric method gives only relative values.

Calculations and Discussion of Errors

If the conductivity decreases linearly with the progress of a second order reaction of the above type, the velocity constant may be calculated from the relation

$$k = \frac{1}{t(a-b)} \log_e \frac{b\left[\frac{a}{b}(C_0 - C_\infty) - C_0 + C_t\right]}{a(C_t - C_\infty)} \quad (6)$$

where a and b are initial concentrations, C_0, C_∞ and C_t are, respectively, the conductivities at the beginning and end of the reaction and at time t. Although such a linear relationship does not necessarily imply constant ionic mobilities, one could hardly expect it to hold for reactions in which two monovalent ions are replaced by a bivalent ion. Since it is practically impossible to make up any given solutions sufficiently accurately to find this deviation from a linear relationship, the following expedient was adopted.

Two solutions were made up as follows:

	(1)	(2)
Sodium hydroxide	0.01 M	0.005 M
Sodium propionate	0.005 M	None
Sodium malonate	None	0.005 M

These are of the same ionic types as our initial and final solutions for reactions (1) to (4) and should show about the same deviations from a linear relationship upon being mixed. They were made up in flasks from which the liquid could be drawn by means of stopcocks. Both flasks and tubes were paraffined, and atmospheric carbon dioxide guarded against by soda-lime tubes. The flasks could be weighed to determine accurately the amount of liquid drawn out. A weighed amount of (1) was put into the apparatus (Fig. 1) while

a stream of hydrogen prevented entrance of air. The entire apparatus was paraffined for this purpose. After the conductivity had been determined, weighed amounts of (2) were added from the other flask. After each addition, the solutions were thoroughly mixed in the apparatus by means of the hydrogen, and the conductivity of the resulting solution measured. The entire procedure was repeated, beginning with solution (2). The deviation when potassium chloride is present was also determined. For this purpose, solutions (1) and (2) were made up from the same potassium chloride solution, although a slight difference in potassium chloride content would make no difference in the results, using the present procedure.

In the following table, the deviation from what would be expected on the basis of a linear law of mixing is given in terms of the per cent. of the total difference in conductivities of (1) and (2):

% of (2)	No KCl	% Deviation 0.022 M KCl	0.05 M KCl
15	+0.35	+0.15	
30	.50	.25	
50	.50	.25	+0.10
70	.40	.20	
85	.25	.15	

The positive sign indicates that the corrections must be added to the observed conductivities to give that expected on the basis of a linear relationship. For more dilute solutions it was assumed that the same correction would apply for the same ratio between potassium chloride and the other substances.

These corrections, interpolated where necessary, were applied to all our time–conductivity curves for reactions (1) to (4) before the k's were calculated by Equation (6). While these corrections are only rough, especially since the propionate ion is substituted for the monoester ion, they are at any rate small, and the effect on the kinetic data shows that the corrections are in the right direction. The "infinite" conductivity was calculated from the final reading by using an approximate value of k. Since the final reading was always close to the "infinite" value, an approximate value of k gives the "infinite" conductivity well within the limits of other errors. Furthermore, a second adjustment was often made from the k calculated from the first "infinite" conductivity. The initial conductivity was taken as that obtained by extrapolation to the time at which the base was added.

Some sample runs are shown in Table I.—The initial concentrations of hydroxyl ion and monoester ion are given by a and b, respectively, and the time is in minutes. Values of k have been calculated from both the "corrected" and observed conductivities. The drift in k with time is undoubtedly due to the increase in ionic strength during the reaction.

TABLE I
SAMPLE RUNS FOR SUCCINIC MONOESTER
$a = 0.00903, b = 0.00454$, no KCl

t	Cond.	Corr.	k(uncorr.)	k(corr.)
0	8526			
10	8322	+5	1.21	1.21
20	8150	8	1.23	1.20
30	7994	9	1.24	1.22
40	7858	10	1.25	1.23
50	7741	10	1.26	1.24
60	7637	10	1.27	1.24
70	7544	10	1.27	1.25
80	7463	10	1.27	1.25
90	7392	10	1.27	1.25
100	7327	9	1.27	1.25
∞	6549			

$a = 0.01012, b = 0.00479$, 0.044 M KCl

t	Cond.	Corr.	k(corr.)
0	29,050		
10	28,740	+1	1.41
20	487	2	1.41
30	270	2	1.42
40	084	2	1.44
50	27,932	2	1.44
60	800	2	1.44
70	683	2	1.44
80	575	2	1.46
90	494	2	1.45
100	427	1	1.43
∞	26,647		

The uncertainty of the time required for mixing is not believed to be serious for reactions (2), (3) and (4). The change in ionic strength during the reaction is more serious. It is believed, however, that the consistency in procedure and calculations largely eliminates the effects of errors on the comparison of the kinetic salt effects for these three reactions.

The dependence of k upon ionic strength for Reactions (2), (3) and (4) is shown in Table II and Fig. 2. The value of k is taken as that calculated from the time when half the ester is used up, as determined from the "corrected" time–conductivity curves, rather than some arbitrary mean. This is conveniently calculated from the relation

$$k = \frac{1}{t_{1/2}(a - b)} \log_e \left(2 - \frac{b}{a} \right)$$

The ionic strengths were arbitrarily assumed to be those at the time when one-fourth of the ester had been saponified.

TABLE II

KINETIC SALT EFFECTS AT 20° FOR REACTIONS (2), (3) AND (4)

	a	b	KCl	k	Log$_{10}$ k	$\sqrt{\bar{\mu}}$
	0.00614	0.00425	None	0.747	$\bar{1}$.873	0.106
	.00896	.00610	0.0105	.787	0.896	.165
(2)	.00951	.00532	.0243	.82$_2$	.915	.201
	.00842	.00604	.0423	.88$_3$	.946	.242
	.00507	.00351	None	.69$_0$	.839	.097
	0.00903	0.00454	None	1.24$_5$	0.095	0.121
	.01012	.00479	0.044	1.44	.158	.246
	.01001	.00493	.022	1.37	.137	.195
(3)	.00488	.002335	.022	1.36	.133	.173
	.00480	.00240	None	1.17$_5$	.070	.088
	.001851	.000856	None	1.11	.045	.054
	0.01040	0.00548	None	1.72	0.236	0.131
	.01006	.00513	.021	1.79	.253	.194
	.01125	.00520	.043	1.92	.283	.246
(4)	.00674	.00270	None	1.57	.196	.103
	.00596	.002425	.022	1.74	.240	.176
	.00300	.001226	None	1.49	.173	.062

The following values of k_0 at 20° were found for these five reactions, the time being in minutes: (1) 23 $\pm$ 1.5, (2) 0.60, (3) 1.01, (4)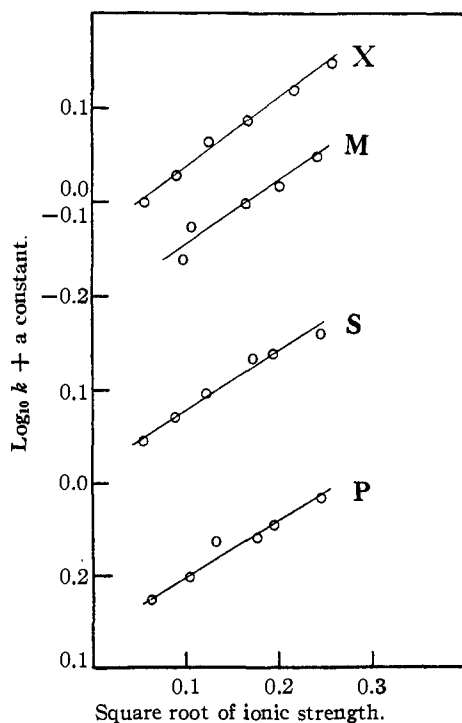 1.36 and (5) 1300. The values for (2), (3) and (4) were found by a linear extrapolation. If the extrapolation had been curved to give the theoretical limiting slope of 45°, the values would have been about 5% less. The values for (1) and (5) are considerably in doubt for reasons given previously.

The Photometric Method

Procedure.—For reactions (1) and (5) it was desirable to find a method which would eliminate the necessity of knowing the time of mixing of the reactants as well as other common errors arising from the use of small concentrations of reactants. Furthermore, a conductivity method cannot be used when the concentration of neutral salt is very large compared to that of the reactants. The method devised was in principle the following. The reactants were mixed in approximately known concentrations, the solution containing also an indicator. The solution was then divided into two parts and neutral salt added to the one part. Time was reckoned from the moment of adding the salt. By measuring the intensities of the color of the indicator as a function of time, the relative times required for the two solutions to reach a certain concentration of hydroxyl ion could be determined. The errors and corrections will be discussed later.

The experiments were carried out at room temperature. A cylindrical vessel for mixing the reactants was fitted with a three-holed stopper. The microburet for adding the base was inserted in the one hole. A tube just through the second hole was joined to a three-way stopcock the other two arms of which were, respectively, open to the atmosphere and connected to the supply of carbon dioxide-free air. A tube through the third hole and reaching to the bottom of the reservoir was joined, by a T-tube, to one side-tube of each of the photometer tubes. These were 25 cm. long with a side-tube near each end and had a capacity of 135 cc. each. The other side-tube of each was connected to a three-way stopcock which was, in turn, connected as the one above. The photometer tubes were in a horizontal position with the side-tubes upward.

About 300 cc. of water containing the ester salt and the indicator was put into the reservoir. Thymolphthalein was used for the oxalic monoester and meta-cresol purple for the betaine ester. The indicator concentration was approximately $3 \cdot 10^{-7}$ molal. That of the ester salt was 0.0025 in case of the oxalic monoester and 0.0001 in case

Fig. 2.—Kinetic salt effect for monoester ions: X, oxalic; M, malonic; S, succinic; P, adipic.

of the betaine compound. The indicator and concentrations of reactants selected were such as to give a set of readings covering most of the range of the indicator and running for about an hour. Carbon dioxide-free air was blown through the photometer tubes and the solution for about two hours, separate bubblers showing proper division of the air. The one tube contained a weighed quantity of sodium or potassium chloride. While the air was still being blown through the solution, the sodium hydroxide was added from the micro-buret. For the oxalic monoester, enough tenth normal base was added to give a concentration of 0.0005 molal, and, for the betaine ester, enough hundredth normal base to give a concentration of 0.00005 molal. An excess of ester salt was thus left at the end of the reaction. Three minutes were allowed to make sure of complete mixing, after which the stopcocks were turned so that the solution was forced into the photo-meter tubes by the carbon dioxide-free air. When the tubes were nearly filled the stopcocks were closed, and the tube containing the salt was rocked to obtain complete mixing. Time was reckoned from the moment the solution entered the tube. Only a few seconds were required for filling. The photometer tubes were disconnected and, after the side tubes had been closed, transferred to the holder in a Zeiss–Pulfrich spectrophotometer. Care was taken throughout to see that the two tubes were kept in as nearly as possible the same environment. An asbestos band around each served for the short time it was necessary to handle them. The holder was made to rotate so that the tubes could be placed alternately in the same beam and compared with a blank placed in the other beam. With the yellow color disk, good absorption was obtained with the indicators in the basic form and practically none with the indicators in the acid form. A typical set of readings is shown in Fig. 3. After the run the amount of solution in the tube containing the neutral salt was determined.

Calculations and Errors

Neglecting corrections, if t_1 and t_2 are the times required for solutions (1) and (2) (solution (2) containing the neutral salt) to reach a certain

color intensity (hydroxyl-ion concentration), counting from the time when the salt was added, then $k_1/k_2 = t_2/t_1$, where the k's denote an average velocity constant over the time considered. A plot of $\log_{10}k$ + a constant against a function of the amount of neutral salt added may thus be obtained.

Three factors requiring corrections or comments immediately suggest themselves: (1) the heat of solution of the salt, making k_2 a velocity constant corresponding to a slightly lower temperature than k_1; (2) the salt effect on the indicator equilibrium, displacing the ratio between the concentrations of the acid and basic forms for a given hydroxyl-ion concentration; and (3) a secondary salt effect, due to a difference in the amounts of
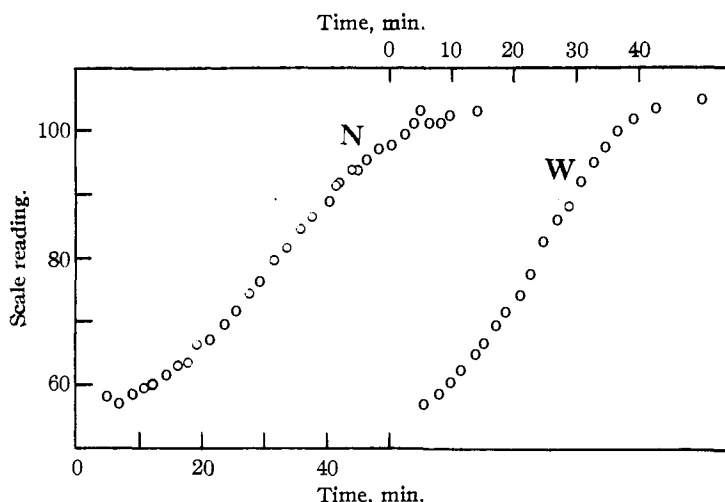

Fig. 3.—Sample run for photometric method: N, tube containing no salt; W, tube containing salt and run simultaneously.

indicator "titrated" in the two solutions up to a certain stage in the reaction. The last of these is believed to be negligible, both because of the low concentration of indicator ($3 \cdot 10^{-7}$ molal) and because the difference in the amounts "titrated" is a rather small part of the total amount of indicator. A simple calculation shows that the cooling effect is negligibly small for the lower concentrations of salt used. For the higher concentrations, an idea of the magnitude of the effect was obtained by comparing the effects of sodium and potassium chlorides, the latter of which has four times the heat of solution of the former. At a concentration of 0.02 molal the difference was found to be, roughly, 2% of the total kinetic salt effect and at 0.06 molal 5%. An idea of the effect of salt on the indicator equilibrium was ob-

tained by running sets of blanks in the same way as the runs for the reactions. Enough base was added to partly change the indicator. Below 0.01 molal salt concentration, the effect was within the limits of error of the photometer readings. At the midpoint of the indicator, the effect was about one scale division at 0.02 molal, 2 divisions at 0.05 molal, and three divisions at 0.2 molal. The effect was about the same for the two indicators and in the direction of a higher concentration of the basic form, as would be expected from the ionic types of these indicators. This effect must not be confused with the usual "salt error" of an indicator, since the latter deals with measurement of hydrogen-ion activity while we are interested in hydroxyl-ion concentration.

Two sample runs are shown in Table III for each of the two esters, one run in each case requiring corrections. The values of t_1 and t_2 are the times in minutes required to reach the given scale reading. All the data on these two compounds are summarized in Table IV and plotted in Figs. 2 and 4. The ionic strengths were taken to be those when three-fourths of the base had reacted, since about half had reacted before the salt was added. The choice of an "average" ionic strength, within reasonable limits, has little effect on these plots, however.
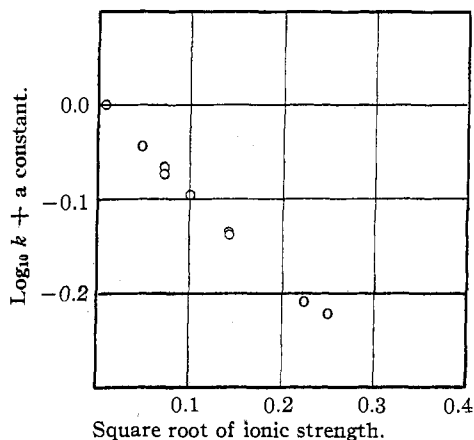

Fig. 4.—Kinetic salt effect for betaine ester.

Discussion

It will be seen that, within the limits of errors, there is no difference in the kinetic salt effects for the four homologous ester ions. The curves are nearly straight lines with a slope somewhat less than the limiting slope of 45° predicted by the Brönsted–Debye formula. Whether the curves approach the theoretical slope at lower concen-

TABLE III
SAMPLE RUNS FOR PHOTOMETRIC METHOD
Oxalic monoester. 0.00515 M NaCl

Scale	t_1	t_2	t_1/t_2
70	26.8	25.2	1.06
75	31.8	29.3	1.085
80	35.6	33.5	1.06
85	39.7	37.0	1.07
90	44.1	41.7	1.06
95	49.7	46.8	1.06

Mean 1.065

$\sqrt{\mu} = 0.092$, $\log_{10} 1.065 = 0.027$

0.0634 M NaCl

Scale	t_1	t_2	t_2 (corr.)	t_1/t_2 (corr.)
70	23.9	17.5	16.9	1.41
75	28.3	20.8	20.2	1.40
80	32.2	23.8	23.2	1.39
85	36.2	26.4	25.9	1.40
90	40.7	29.3	28.9	1.41
95	45.8	32.6	32.4	1.41

Mean 1.40

$\sqrt{\mu} = 0.258$, $\log_{10} 1.40 = 0.146$

Betaine Ester
0.00217 M KCl

Scale	t_1	t_2	t_2/t_1
70	20.2	18.1	1.116
75	25.0	22.1	1.13
80	29.7	26.7	1.11
85	34.6	31.6	1.09

Mean 1.11

$\sqrt{\mu} = 0.0475$, $\log_{10} 1.11 = 0.045$

0.0493 M KCl

Scale	t_1	t_2	t_2 (corr.)	t_2 (corr.)/t_1
70	15.6	27.9	25.0	1.60
75	20.0	35.6	32.6	1.63
80	24.2	42.2	39.5	1.63
85	28.8	48.7	46.5	1.61
90	33.8	56.4	54.6	1.61

Mean 1.62

$\sqrt{\mu} = 0.222$, $\log_{10} 1.62 = 0.210$

TABLE IV
KINETIC SALT EFFECTS FOR REACTIONS (1) AND (5)

| NaCl Molality	(1) $\sqrt{\mu}$	(1) $\log_{10} k + C$	KCl Molality	(2) $\sqrt{\mu}$	(2) $\log_{10} k + C$
None	0.057	0	None	0.009	0
0.00515	.092	0.027	0.00217	.047	−0.045
.01256	.126	.062	.00493	.071	.075
.02512	.168	.086	.00501	.071	.070
.0440	.217	.116	.0100	.010	.096
.0634	.258	.146	.0202	.142	.139
			.0202[a]	.142	.135
			.0493	.222	.210
			.0628[a]	.250	.223

[a] NaCl.

trations[3] cannot be told from our data. These data, therefore, neither prove nor disprove the suggestion made by La Mer and Greenspan that

the theoretical slope may not be reached even in the limit. The betaine compound, however, gives the theoretical slope for values of $\sqrt{\mu}$ below 0.1, within the limits of error.

The Reactions between Brominated Organic Ions and Thiosulfate

Since it was the apparently anomalous kinetic salt effects in the reactions between β-bromopropionate, bromomalonate, and bromosuccinate ions, respectively, and thiosulfate ion that stimulated this paper, a simple investigation of these reactions was made, using the β-bromopropionate and bromosuccinate only. Besides the reaction involving substitution of the bromine by thiosulfate

$$^-OOCCHBrCH_2COO^- + S_2O_3^- =$$
$$\begin{array}{c} S_2O_3^- \\ | \\ ^-OOCCHCH_2COO^- + Br^- \end{array} \quad (7)$$
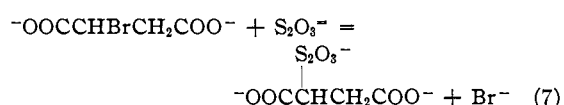
there is the concurrent reaction with the water, forming hydrobromic acid

$$^-OOCCHBrCH_2COO^- + H_2O =$$
$$^-OOCCHOHCH_2COO^- (?) + H^+ + Br^- \quad (8)$$
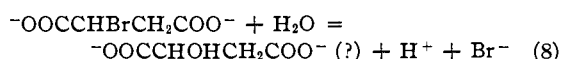
It is known, however,[1] that the rate of formation of acid is very much lessened by the presence of

thiosulfate, and this reaction was, therefore, ignored in the previous studies[1,2] of kinetic salt effect. It does not seem plausible that one reaction could be retarded appreciably by the mere presence of another. It was thought, therefore, that the mechanism by which the formation of acid was prevented may be the chief complicating factor which, together with the concentration of reactants used, would yield a set of k's that decreased with increasing ionic strength. It was decided to follow both the rate of formation of acid and that of disappearance of thiosulfate, varying the relative amounts of reactants from a large excess of one to a large excess of the other, keeping the initial ionic strength the same in all experiments. The experiments were made at 20° and simple chemical procedure was used, that is, removal of samples and titration with standard iodine and sodium hydroxide solutions, the titers just after mixing being taken as blanks. Tables V and VI show the initial concentrations used. The differential coefficients were calculated graphically from the time–concentration curves. The unit of time is one hundred hours. While no high degree of accuracy is claimed for these figures, it is at once apparent that the reactions are not

TABLE V

BROMOSUCCINATE–THIOSULFATE REACTION AT 20°

Run	BrSuc⁻	S₂O₃⁻	$-d(S_2O_3^-)/dt$	$d(HBr)/dt$
1	0.002	0.013	$0.0042 = 161(BrSuc^-)(S_2O_3^-)$	$0.0003 = 0.15(BrSuc^-)$
2	.005	.01	$.0130 = 260(BrSuc^-)(S_2O_3^-)$	$.0008 = .16(BrSuc^-)$
3	.0075	.0075	$.0150 = 267(BrSuc^-)(S_2O_3^-)$	$.0018 = .24(BrSuc^-)$
4	.011	.004	$.0163 = 370(BrSuc^-)(S_2O_3^-)$	$.0034 = .30(BrSuc^-)$
5	.015	.001	$.0054 = 360(BrSuc^-)(S_2O_3^-)$	$.0065 = .43(BrSuc^-)$
6	.014	None		$.0069 = .49(BrSuc^-)$

TABLE VI

β-BROMOPROPIONATE–THIOSULFATE REACTION AT 20°

Run	BrPr⁻	S₂O₃⁻	KCl	$-d(S_2O_3^-)/dt$	$d(HBr)/dt$
1	0.002	0.011	None	$0.0009 = 40(BrPr^-)(S_2O_3^-)$	
2	.005	.01	None	$.0027 = 54(BrPr^-)(S_2O_3^-)$	
3	.0075	.0075	0.0075	$.0048 = 85(BrPr^-)(S_2O_3^-)$	$0.00013 = 0.02(BrPr^-)$
4	.01	.004	.013	$.0058 = 145(BrPr^-)(S_2O_3^-)$	$.0005 = .05(BrPr^-)$
5	.014	.0009	.017	$.0047 = 370(BrPr^-)(S_2O_3^-)$	$.0027 = .20(BrPr^-)$
6	.015	None	.02		$.0057 = .38(BrPr^-)$

TABLE VII

"SECOND ORDER CONSTANTS" FOR RUNS OF TABLE V, $b = (S_2O_3^-)$

	Run 1		2		3		4		5	
t hr.	b	k	b	k	b	k	b	k	b	k
6.3	0.01277	1.5	0.00928	2.5	0.00645	3.4	0.00303	4.2	0.00065	4.6
12.9	.01243	2.0	.00834	3.4	.00561	3.5	.00195	5.7	.00032	6.1
23.9	.01210	2.0	.00725	4.0	.00385	5.3	.00081	7.6	.00005	9.9
45.1	.01188	1.5			.00252	5.8				

The bromosuccinate concentrations were not corrected for the water reaction. Even if the k's, already calculated from a function whose derivation depends on the constancy of the k's, could be "corrected" for this factor, the drift would not be seriously affected.

second order and that the "second order k's" obtained increase with increased ratio of brominated ion to thiosulfate. This is shown further in Table VII. The increase in k with time is greatest where the ratio of bromosuccinate to thiosulfate increases the most with time. There seems to be, also, a factor beside the reactant ratio, giving low values of k in the first stages. In the previous investigations[1,2] an excess of thiosulfate was always used. Bedford, Mason and Morrell[2] obtained a consistent decrease in k with time in each run of the bromosuccinate reaction and La Mer and Kamner[1] obtained no consistent drift with the β-bromopropionate. It is evident that such would very likely be the case with an excess of thiosulfate, for this sort of deviation from second order, especially if readings were not taken in the first stages.

While no attempt will be made here to account for the present data, a few calculations will be made to show how an apparent negative salt effect may be obtained for a reaction which is assumed second order but is only partly so. In the above mentioned studies[1,2] on these reactions, the ionic strength was varied only by varying the concentrations of reactants, and not by the use of neutral salts. The initial concentration of thiosulfate was also about twice that of the brominated ion in each run. If we assume the following equation for the rate of disappearance of thiosulfate, which holds roughly over a limited range

$$-d(B)/dt = k_1(A) + k_2(A)(B) \qquad (9)$$

(A) denoting the concentration of the organic ion, then round values of k_1 and k_2 are, respectively, unity and 150 for the bromosuccinate and 0.3 and 30 for the β-bromopropionate. To show how this would lead to an apparent decrease in the values of k, calculated as for second order reactions, with increasing ionic strength, the following table has been calculated. The values of $-d(B)/dt$ were calculated from Equation (9), and the values of "k" are those obtained on the supposition that the reaction is second order.

(B)	(A)	$-d(B)/dt$	"k"	
0.05	0.025	0.212	170	$k_1 = 1$
.01	.005	.0125	250	$k_2 = 150$
.002	.001	.0013	650	
.05	.025	.045	36	$k_1 = 0.3$
.01	.005	.003	60	$k_2 = 30$
.002	.001	.00036	180	

It was hoped that a simple explanation could be found to account simultaneously for the deviations from second order and the effect of thiosulfate on the rate of acid formation (see Tables V and VI). This seems to be impossible without an extensive and accurate study of these reactions.[12]

In order to see whether neutral salts increase the velocity constants of these reactions, in accordance with Brönsted's theory, solutions corresponding to those of run 2 in Tables V and VI were made up and divided into three parts each. Dry potassium chloride was added to two of these to give the concentrations shown in Table VIII, and the solutions placed in the thermostat at 20°. The differential coefficients were calculated as above, the unit of time being one hundred hours.

TABLE VIII

EFFECT OF KCl

KCl, M	$-d(S_2O_3^-)/dt$	
None	0.0130	
0.1	.0151	BrSuc
.2	.0165	
None	.0027	
0.1	.0029	BrPr
.2	.0030	

The effect, although very small, is at least not of the opposite sign from that expected on the basis of Brönsted's theory. At present, therefore, it cannot be said that these reactions are either clear-cut or a definite contradiction to the Brönsted theory. Essentially the same point of view has been expressed by Professor La Mer in a private communication.

Summary

1. The kinetic salt effect was studied by a conductivity method for the saponification of the monoethyl esters of malonic, succinic, and adipic acids, and by a photometric comparison method for monoethyloxalic ester and the betaine ester $(Et_3NCH_2COOEt)ClO_4$.

2. Within the limits of experimental error,

(12) The writer has been informed recently by Professor La Mer, in a private communication, that the β-bromopropionate reaction has been under investigation for some time by him and Dr. Greenspan.

no effect of the distance of the reacting group from the charge could be found for the four homologous ions.

3. The kinetic salt effect for the saponification of the betaine ester was studied down to ionic strength 0.0001 and was found to be that given by the Brönsted–Debye equation for values of $\sqrt{\mu}$ below 0.1.

4. Calculations were introduced to show how certain deviations from second order can lead to an apparent negative kinetic salt effect, and an attempt was made to show how such deviations could account for certain previously reported kinetic salt effects in the opposite direction from that expected from Brönsted's theory.

Raman Spectrum of Rubber and Some Related Hydrocarbons

BY S. D. GEHMAN AND H. J. OSTERHOF

The Raman spectra of organic compounds have been used very extensively in studying their structure and the method has been applied for the solution of some difficult problems of constitution. The extension to highly polymerized materials has been very limited, although it offers a means of gaining information about the primary chemical linkages without disturbing the secondary forces. Signer and Weiler[1] showed that polysterol gave a strong line spectrum in which the frequencies were practically identical with those of ethylbenzene, the unit of structure in the long chain molecules. They showed, furthermore, that the frequencies were the same in the solid state and in solution, for this polymer, indicating an independence from the micellar forces.

The Raman spectrum has not been used at all, previously, for the study of rubber or related high polymers, attempts to secure a line spectrum leading only to bands and background.[2,3,4] The difficulties and ambiguities in the deduction of the original structure of rubber from chemical reactions should make welcome any insight which can be gained by the application of this newer method.

The Raman spectra of series of organic compounds show that certain frequencies can be ascribed to the various primary organic linkages. Some of these frequencies are remarkably independent of the rest of the structure of the molecule. This property renders possible the use of the Raman spectrum to study the primary linkages in highly polymerized materials, since the frequency will depend not upon the size of the molecule but upon the unit of structure. The various linkages can then be identified by comparison with those of simpler, related structures.

The results to be obtained from a study of the Raman spectra of such materials as rubber and its derivatives promise to be extremely interesting, but the work has been hampered by the presence of a continuous background which we have not been able to eliminate entirely. Signer and Weiler[1] have mentioned the possibility that each molecule of a high polymer possesses a fluorescent end group and have even suggested the measurement of the continuous background intensity as a means for estimating the average molecular size. They admitted, however, as an equally probable alternative, that the background might be caused by fluorescent impurities. It would be interesting to determine for rubber, with the fluorescence microscope, whether the fluorescence occurred in the sheath of the latex particle. Another difficulty encountered in this work is the almost necessary limitation of having to work with solutions and gels thus reducing the Raman intensities due to the dilution. Crystal powder methods[5] might be applicable but they do not seem very promising unless the source of light is entirely free of a continuous spectrum.

Apparatus and Method

The apparatus was of the conventional type for Raman studies of liquids and is sketched in Figs. 1 and 2. The light source was a quartz mercury arc and the spectrograph a Bausch and Lomb No. 2700 constant deviation instrument. The cells were constructed from Pyrex tubing as shown in Fig. 1, having rubber packing at the ends overlaid with a thin coating of acid-proof cement. The arc

(1) Signer and Weiler, Helv. Chim. Acta, 15, 649 (1932).

(2) Franklin and Laird, Phys. Rev., 36, 147 (1930).

(3) Busse, J. Phys. Chem., 36, 2862 (1932).

(4) Gehman, THIS JOURNAL, 57, 1382 (1935).

(5) Kohlrausch, "Der Smekal Raman Effekt," Verlag Julius Springer, Berlin, 1931, p. 37.