and hydrolysis of the product to hydrocinnamic acid which was identified by a mixture m. p. of its anilide.

Ethyl *p*-Ethoxybenzoylacetate (Example of method B).—Diethyl carbonate (500 ml.) and *p*-ethoxyacetophenone (82 g.) were placed in a 1-liter, 3-necked flask, arranged as described above. The reaction mixture was stirred, heated to refluxing, and a solution of sodium ethylate made from sodium (12 g.) and anhydrous ethyl alcohol (250 ml.) was added slowly from the dropping funnel, while alcohol was removed simultaneously as distillate at the head of the column. When no more alcohol was obtained as distillate the reaction mixture was cooled and poured onto a mixture of ice and hydrochloric acid. The organic layer was separated, washed free of acid, dried over calcium chloride and distilled until all diethyl carbonate had been removed. Since the residue tended to decompose when distillation was attempted at 2 mm. pressure, the product was purified by means of its copper salt. The residue was mixed with alcohol (100 ml.) and treated with a saturated, aqueous solution of copper acetate until no more precipitate formed. The green solid was filtered off and washed with alcohol. It was decomposed with a solution of acetic acid in the presence of ether and the ether layer was washed with water until free of copper. Evaporation of the ether yielded an oil which solidified and was recrystallized from a mixture of ether and petroleum ether; m. p. 50–53°, yield 38% (45 g.). After sublimation in a high vacuum at 87°, the m. p. was 53–54°.

Anal. Calcd. for $C_{13}H_{16}O_4$: C, 66.1; H, 6.8. Found: C, 66.2; H, 6.8.

The keto ester was converted to 3-*p*-ethoxyphenyl-5-isoxazolone, m. p. 135–136°, by reaction with hydroxylamine.

Anal. Calcd. for $C_{11}H_{11}O_3N$: N, 6.8. Found: N, 6.8.

The keto ester was converted to 3-*p*-ethoxyphenyl-1-phenyl-5-pyrazolone, m. p. 152–153°, by reaction with phenylhydrazine.

Anal. Calcd. for $C_{17}H_{16}O_2N_2$: N, 10.0. Found: N, 10.0.

Ester of β-Keto-γ-methylvaleric Acid (Example of method C).—Methyl isopropyl ketone (50 g.) and diethyl carbonate (300 ml.) were stirred mechanically in a 500-ml. 3-necked flask and cooled to 2°. Alcohol-free sodium methylate (29 g.) was made into a thick paste with diethyl carbonate and added slowly to the reaction mixture. After two hours the reaction mixture was warmed and as much alcohol as possible fractionated out under a pressure of 200 mm. After cooling, the residue was acidified with acetic acid, agitated with water, and the organic layer was separated and fractionated. After removal of the excess diethyl carbonate an ester fraction was obtained boiling at 70–81° at 10 mm. and weighing 21.6 g. This was a mixture of methyl and ethyl esters of β-keto-γ-methylvaleric acid. An alcoholic solution of the product gave a red color when treated with a little ferric chloride, indicating the presence of an enolic group. The ester was converted to 3-isopropyl-1-phenyl-5-pyrazolone by reaction with phenylhydrazine. The product was sublimed in a high vacuum at 80° and then melted at 81–83°.

Anal. Calcd. for $C_{12}H_{14}ON_2$: C, 71.2; H, 7.0; N, 13.8. Found: C, 71.9; H, 7.0; N, 13.9.

Summary

A procedure is described for condensing alkyl carbonates with ketones by means of metal alcoholates to give β-keto esters. The new method has been applied to a variety of ketones.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rate and Mechanism in the Reactions of Ethyl *p*-Toluenesulfonate with Water, Hydroxyl Ions and Various Halide Ions[1]

BY HAROLD R. MCCLEARY AND LOUIS P. HAMMETT

It is so generally true that, in a series of similarly constituted compounds, the rate of reaction parallels the thermodynamic stability that the exceptions are of special interest. This is all the more so because such exceptions must lie back of many important cases of homogeneous catalysis and many puzzling phenomena in the field of the Walden inversion.[2] The reactions of the alkyl halides offer a particularly striking example of this kind of exception, an example which is here extended by a quantitative study of the reactions of ethyl toluenesulfonate, which are closely related to the reactions of the alkyl halides.

The reactions investigated were the water reaction

$$C_7H_7SO_2OC_2H_5 + 2H_2O \xrightarrow{k_1} C_7H_7SO_2O^- + H_3O^+ + C_2H_5OH \quad (A)$$

and the displacements by hydroxyl ion (B) and halide ion (C)

$$C_7H_7SO_2OC_2H_5 + OH^- \xrightarrow{k_2} C_7H_7SO_2O^- + C_2H_5OH \quad (B)$$

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[1] Dissertation submitted by Harold Russell McCleary in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science, Columbia University.

[2] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 182.

$$C_7H_7SO_2OC_2H_5 + X^- \underset{k'_{-2}}{\overset{k'_2}{\rightleftarrows}} C_7H_7SO_2O^- + C_2H_5X \quad (C)$$

The ethyl halide solvolysis

$$C_2H_5X + 2H_2O \xrightarrow{k_3} C_2H_5OH + H_3O^+ + X^- \quad (D)$$

also was measured.

All kinetic measurements were made at 50.000 ± 0.005° in a dioxane–water medium containing 60.72% dioxane by weight. The dioxane made the reacting systems homogeneous without introducing additional reaction possibilities.

Experimental

Apparatus.—Only calibrated weights and volumetric apparatus were used. The temperature was determined by a thermometer calibrated by the Bureau of Standards.

Ethyl *p*-Toluenesulfonate.—Eastman Kodak Company "Practical" grade was twice distilled under vacuum through a 20-cm. Vigreux column wrapped with asbestos, the first and final fifths being rejected each time; the boiling point was 145° at approximately 4 mm. This sample was partially crystallized repeatedly without solvent; the crystals were permitted to form very slowly by allowing the melt to stand at room temperature until approximately three-fourths was crystallized. The degree of purification was determined by measuring the cooling curves of the various fractions. The apparatus consisted of a six inch by one inch test-tube fitted with a small glass stirrer and a thermometer graduated in tenths of a degree. The test-tube was so insulated that a temperature gradient of 10° at room temperature permitted a rate of cooling of 0.5° a minute. The material accepted as pure gave a cooling curve which remained constant within 0.05° out to half crystallization; m. p. 32.2–32.3°. Titration of the acid formed on complete hydrolysis indicated 100.3% purity. Rate measurements made on a fraction which melted at 31.9–32.0° agree within experimental error with those made on the pure material, showing that the impurity does not affect the quantities which are measured in this investigation.[3]

Sodium *p*-Toluenesulfonate.—A saturated solution of ethyl *p*-toluenesulfonate in a dioxane–water solution containing about 60% dioxane by volume was permitted to stand for two weeks at 50°; complete hydrolysis of the ester was further assured by heating the solution on the steam-bath for two days. The acidity of this solution was titrated and it was then exactly neutralized with sodium hydroxide solution. On concentrating and cooling, crystals of the dihydrate were obtained from the mother liquor. These were dehydrated over phosphorus pentoxide. The product contained no measurable amount of free acid or alkali and gave no test for sulfate with barium chloride. An analysis for sodium gave: calcd., 11.84; found, 11.95.

The Halide Esters.—Eastman Kodak Company best grade of these materials was used. Ethyl chloride was used directly; the reported boiling point is 12.5–13.0°. On complete hydrolysis of this ester an analysis for chloride showed it to be 100.3% pure. Ethyl bromide was distilled over phosphorus pentoxide through an 18-in. column the middle fraction only being retained; b. p. 38.0–38.2°.

Ethyl iodide was washed with water, dried over calcium chloride, and distilled through an 18-in. column the middle fraction only being retained; b. p. 72.2–72.3°.

The Halide Salts.—Only materials meeting A. C. S. specifications were used. Sodium chloride was reprecipitated from hydrochloric acid solution, fused in a platinum crucible, pulverized in an agate mortar, dried at 120° and stored over phosphorus pentoxide. Analysis for halide corresponded to 99.8% sodium chloride. Potassium bromide was crystallized twice from water solution and dried at 120°; subsequent analysis showed the presence of 0.4% chloride assuming all halide impurity to be chloride. This checks with the analysis on the label, indicating that recrystallization does not remove the impurity. Potassium iodide was used directly after grinding in an agate mortar and drying at 120° for two hours. Analysis for halide calculated as iodide gave 100.0% potassium iodide.

Other Materials.—1,4-Dioxane (Carbide and Carbon Chem. Co.) was purified in 2–3 liter quantities as described by Beste and Hammett.[4]

Sodium perchlorate solution was prepared from Mallinckrodt A. C. S. grade perchloric acid 99.8% neutralized with carbon dioxide-free sodium hydroxide solution. Tests on this solution showed no detectable trace of chloride.

Primary standards for titration were Bureau of Standards acid potassium phthalate and the highest grade of mercuric oxide which was reprecipitated, dried over phosphorus pentoxide for two weeks, and stored in the dark. These standards were checked to two parts per thousand against each other by analysis of a solution of hydrochloric acid.

Analyses for chloride, bromide and iodide were made with 0.025 *N* mercuric nitrate using diphenylcarbazide indicator. The validity of the method for chloride determinations has been established by Roberts[5]; the extension of the method to the determination of bromide and iodide is reported elsewhere.[6]

Method.—All kinetic experiments were made in a dioxane–water medium containing 60.72% dioxane by weight. This solvent was prepared according to the method described previously.[4] In the case of experiments containing sodium hydroxide and/or sodium perchlorate these solutes were introduced as solutions at the time the solvent was prepared, and correction was made for the amount of water displaced by these solutes. All other solutes were weighed out and added directly. In starting experiments on the reaction of ethyl toluenesulfonate with water, hydroxyl ion, chloride ion and bromide ion the general procedure was to place the reaction bottle containing the solvent with all solutes except the ester in the thermostat to reach temperature equilibrium; the ester was then added and the initial time taken. Samples for analysis were withdrawn at convenient intervals using a 5-cc. pipet. The weights of a given reaction mixture delivered

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[3] Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, pp. 40 ff.

[4] Beste and Hammett, THIS JOURNAL, **62**, 2481 (1940).

[5] Roberts, *Ind. Eng. Chem., Anal. Ed.*, **8**, 365 (1936).

[6] McCleary, work to be published.

by the dried pipet initially at room temperature were reproducible to 0.1% if the filling was completed within a few seconds. With the exception of the displacement by hydroxyl ion, the above reactions were slow enough to be arrested when the sample was run into a dioxane–water solution at room temperature. The hydroxyl ion reaction was stopped by pipetting the sample into an excess of standard hydrochloric acid solution.

In the case of the iodide reaction the above procedure could not be followed since an acidified iodide solution is easily oxidized by both air and peroxides of the dioxane; instead, the solvent containing all solutes except the ester was cooled to approximately −10°, the ester was added and portions of this reaction mixture were placed in several 10-cc. ampoules and frozen solid in a dry-ice-bath. The ampoules were then evacuated, the frozen solution was remelted under vacuum, then frozen again, and the ampoules reëvacuated and sealed. This procedure was found necessary to remove the air which was trapped during the first freezing. The initial time was taken when the ampoules for a given experiment were placed in the thermostat. The reaction which took place in the one hour necessary to seal the solution in ampoules is negligible since the reaction mixture was frozen solid for all but ten minutes of the hour. The procedure in taking samples for analysis was to remove an ampoule from the 50° bath and plunge it into ice water; it was then brought quickly to room temperature, broken, the contents carefully shaken out and a 5-cc. sample withdrawn for titration. Experiments carried out in this manner showed only a small amount of oxidation of iodide to iodine over a period of twenty-four hours.

If dioxane, which has been freshly distilled from sodium, is permitted to stand in contact with air, it remains free from detectable quantities of peroxides for only thirty-six hours; hence the solvent for the iodide reaction must be freshly prepared. The presence of peroxides does not affect the results of the other experiments as was shown by using an aged solvent in certain cases.

In the halide displacement reactions titrations were made for both acid and halide. With the exception of the ethyl halide solvolyses, all reactions were followed until 40 to 80% complete.

In the experiments on the solvolysis of ethyl chloride and ethyl bromide these esters were sealed and weighed in tared thin glass bulbs blown from 6-mm. tubing. The procedure was to deliver an approximate amount of the cooled ester into the tared bulb through the 6-mm. neck which was three to four inches long; bulb and contents were cooled to the temperature of dry-ice and the neck sealed quickly in an oxygen flame, preserving the portion of the neck which was pulled off to be weighed with the sealed bulb. This technique was found to be an accurate method of weighing out small quantities of very volatile liquids. In starting an experiment the solvent was cooled to −8 to −10° when the bulb containing the ester was broken beneath the surface; this reaction mixture was then sealed in several 10-cc. ampoules as just described for the ethyl toluenesulfonate–iodide reaction.

In spite of the low temperature maintained during this procedure some difficulty was experienced in avoiding loss of small amounts of ethyl chloride; the specific rate determinations are therefore less exact.

In the ethyl iodide solvolysis experiments the weighing of the ester was somewhat of a problem. The use of a weight buret left doubt as to how much ester was lost by evaporation, whereas the thin bulb technique required special care to avoid decomposition when the bulb was sealed. Duplicate experiments were carried out employing both methods and the results are in good agreement.

The course of the ethyl halide reactions was equally well followed by titrations of either acid or halide ion. In ethyl bromide and ethyl iodide reaction mixtures containing sodium toluenesulfonate, titrations for both acid and halide ion were made to detect any displacement of halide ion by toluenesulfonate ion.

In order to examine the possibility of olefin formation during the hydrolysis of ethyl toluenesulfonate the following experiment was performed. An ampoule containing a solution of the half-hydrolyzed ethyl toluenesulfonate was broken in a filter flask the side-arm of which was connected to two glass traps in train; the first trap was immersed in a dry-ice-bath, the second in liquid nitrogen. Hydrogen gas was bubbled through the solution in the filter flask for one hour with vigorous shaking; dissolved ethylene was thus swept through both traps and was condensed in the liquid nitrogen trap. The material condensed in this trap was evaporated by warming to room temperature and transferred to a gas buret. Analysis for olefin was carried out by shaking the gas with bromine and sodium hydroxide solution in Hempel gas pipets according to standard procedure. This method of freezing out the olefin was found to be reliable in the detection of 80% of the olefin in illuminating gas.

Results of duplicate analyses show no detectable amount of olefin formed in the simple hydrolysis of ethyl toluenesulfonate in the dioxane–water solvent.

Rate Calculations.—The following abbreviations will be used in this section: a is initial concentration of ethyl toluenesulfonate, b initial concentration of hydroxyl ion, x concentration of acid at time t, t time in seconds. The ethyl group will be written Et, the toluenesulfonate group Ts, and halide ion X^-.

Data for the water reaction (A) in the complete absence of electrolytes or in the presence of sodium perchlorate or sodium toluenesulfonate were calculated according to the equation $\ln a/(a - x) = k_1t$. The slope of a plot of $\ln(a - x)$ against t increased slightly during the course of a given experiment. For purposes of comparison the initial values of k_1 were obtained from the empirical equation $-\ln(a - x) = -\ln a + k_1t + k_1't^2$; the coefficients of this equation were calculated by the method of averages,[7] whereby adjacent experimental points were used to obtain each of the three simultaneous equations.

In the presence of halide salts reaction (C) is superimposed on (A) and reaction (D) must also

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[7] Daniels, "Mathematical Preparation for Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 235.

be considered. The slope of a plot of $\ln(a - x)$ against time is given by

$$\frac{\mathrm{d}\ln(a-x)}{\mathrm{d}t} = -\frac{1}{a-x}[k_1[\mathrm{EtTs}] + k_3[\mathrm{EtX}]] \quad (1)$$

When t is zero, this equation becomes

$$\left(\frac{\mathrm{d}\ln(a-x)}{\mathrm{d}t}\right)_0 = -(k_1)_0 \quad (2)$$

This initial slope, $(k_1)_0$, was determined by a method of graphical differentiation as follows. A smooth curve was drawn through the experimental points with the aid of a spline such as is used in drafting work. The values of $\ln(a - x)$ at several evenly spaced intervals were read from this curve. The ratio of the differences $\Delta \ln (a - x)/\Delta t$ when plotted against the values of $(t_1 + t_2)/2$ gives a plot of the first derivative of the original curve; by extrapolating to zero time one obtains the value of $(k_1)_0$ given by equation (2). In some experiments where $\mathrm{d}\ln(a - x)/\mathrm{d}t$ does not change very rapidly it was found convenient to calculate an empirical equation by the method of averages described above.

The specific rate of displacement by halide ion, k'_2, was calculated by two methods. The first employs the equation for the rate of decomposition of ethyl toluenesulfonate given by

$$-\mathrm{d}[\mathrm{EtTs}]/\mathrm{d}t = k_1[\mathrm{EtTs}] + k'_2[\mathrm{EtTs}][\mathrm{X}^-] \quad (3)$$

This equation may be written in the form

$$-\mathrm{d}[\mathrm{EtTs}]/\mathrm{d}t = k'[\mathrm{EtTs}] \quad (4)$$

where

$$k' = k_1 + k'_2[\mathrm{X}^-] \quad (5)$$

Values of k' were obtained from a plot of $\ln[\mathrm{EtTs}]$ against time using the method of graphical differentiation described above. Using the value of $(k_1)_0$ from equation (2), values of $(k'_2)_0$ were evaluated from equation (5) for each halide run.

The second method depends on the rate of decrease of halide ion given by

$$-\mathrm{d}[\mathrm{X}^-]/\mathrm{d}t = k'_2[\mathrm{EtTs}][\mathrm{X}^-] - k_3[\mathrm{EtX}] \quad (6)$$

When t is zero this equation becomes

$$-\left(\frac{\mathrm{d}\ln[\mathrm{X}^-]}{\mathrm{d}t}\right)_0 = (k'_2)_0[\mathrm{EtTs}] \quad (7)$$

Plotting $\ln[\mathrm{X}^-]$ against time and calculating the slopes by graphical differentiation one may evaluate $(k'_2)_0$ from equation (7) by extrapolation of the slope curve. The value of $(k'_2)_0$ accepted as correct is a weighted average of these two methods, weight being given to the method with the lowest apparent error.

In the presence of hydroxyl ion we are concerned with reactions (A) and (B). The rate of decomposition of ethyl toluenesulfonate is given by

$$-\mathrm{d}[\mathrm{EtTs}]/\mathrm{d}t = k_1[\mathrm{EtTs}] + k_2[\mathrm{EtTs}][\mathrm{OH}^-] \quad (8)$$

which may be written

$$-\mathrm{d}[\mathrm{EtTs}]/\mathrm{d}t = k''[\mathrm{EtTs}][\mathrm{OH}^-] \quad (9)$$

where

$$k'' = k_2 + k_1/[\mathrm{OH}^-] \quad (10)$$

This value of k'' may be obtained by graphical differentiation of a plot of $\frac{1}{a-b}\ln\frac{[\mathrm{EtTs}]}{\mathrm{OH}^-}$ against time. The value of $(k_2)_0$ may then be evaluated from equation (10) using the $(k_1)_0$ independently determined from hydrolysis measurements. The appropriate value of $(k_1)_0$ must be chosen here since it was found to be somewhat sensitive to changes in the concentration of ethyl toluenesulfonate. No correction however need be made for electrolyte effect in this hydroxide solution since the value of $(k_1)_0$ is unchanged by the presence of sodium perchlorate.

Equation (8) may be also treated as was equation (3) for the halide displacement by plotting $\ln[\mathrm{EtTs}]$ against time; the slope of this curve at any point is given by

$$k''' = k_1 + k_2[\mathrm{OH}^-] \quad (11)$$

The graphical differentiation procedure applied here provides a second method for determining $(k_2)_0$. Except in experiments where a and b were nearly equal, both of these methods were employed.

While it is recognized that the two methods of calculation of k_2 and k'_2 for the hydroxyl and halide ion displacements, respectively, are not completely independent experimentally, it may be pointed out that from the standpoint of exercising judgment in performing the graphical differentiation on two different curves the methods may be regarded as independent and serve as a check on each other.

The specific rates of solvolysis of the ethyl halides, k_3, were determined graphically as the slopes of plots of $\ln[\mathrm{EtX}]$ against time. These slopes are constant over the first 20% of the reaction and thereafter seem to drift slightly downward although the significance of this drift may be neglected here in view of the experimental error involved.

In order to determine whether or not reaction (C) is reversible, experiments were performed on the ethyl halide solvolyses in the presence of sodium toluenesulfonate. If toluenesulfonate ion reacts with ethyl halide, the halide ion concentration should increase faster than the concentration of acid and the difference $[X^-] - [H_3O^+]$ is the concentration of ethyl toluenesulfonate at time *t*. In such a reaction system the rate of change of ethyl toluenesulfonate concentration is given by

$$d[EtTs]/dt = k_{-2}[EtX][Ts^-] - k_2'[EtTs][X^-] - k_1[EtTs] \quad (12)$$

At zero time this equation becomes

$$\left(\frac{d[EtTs]}{dt}\right)_0 = (k'_{-2})_0[EtX][Ts^-] \quad (13)$$

Smooth curves were drawn for both halide and oxonium ion concentrations at time *t*. The function $([X^-] - [H_3O^+])/t$ plotted against *t* and extrapolated to zero time gives an approximate value for $(d[EtTs]/dt)_0$ from which $(k'_{-2})_0$ may be calculated by equation (13).

Errors.—Since the results of this research are based on the determination of initial slopes of curves, it is difficult to estimate the precision with which specific rates are known. However, the distribution of values of $(k_1)_0$ from Table IV plotted in Fig. 1 indicates an average deviation of 1.0%. The estimation of the error in all other rate constants is less exact; it involves a consideration of duplicate experiments as well as a comparison of two methods of calculation in certain cases. Careful examination of the data indicates that no larger error than 2.0 to 2.5% is to be expected except in a few experiments. The specific rates of the first and last two experiments of Table VI may be in error by 4 to 5%, while constants for the displacement by chloride ion may be in error by 6 to 8% because of the difficulty in measuring small slopes and because of the small differences involved in determining $(k_2')_0$ from equation (5). For the ethyl chloride reaction the average of the three values of $(k_3)_0$ listed is correct only to within 20%; this error is believed to be due to unavoidable loss of ethyl chloride.

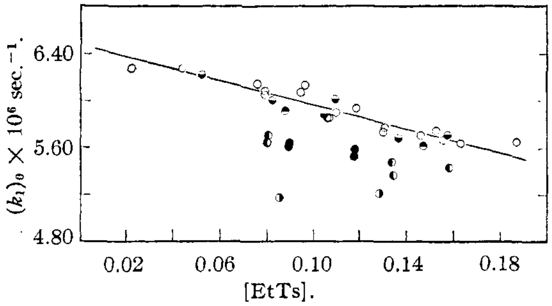

Fig. 1.—Initial specific rates of solvolysis of ethyl toluenesulfonate in dioxane–water medium: ○, no added salts; ◒, in presence of $NaClO_4$; ◓, in presence of NaTs; ●, in presence of NaCl; ◐, in presence of KBr; ◑, in presence of KI.

Sample Data.—For the sake of uniformity and and in order to avoid complications due to unpredictable changes in reaction media, the constants reported in the tables of results are those at the initial time. It is, however, of some importance to see how the specific rate changes during the course of a reaction; a skeleton record is therefore given for a typical experiment on each of the ethyl toluenesulfonate reactions studied (Tables I, II and III).

In Table I the values of k_1 were calculated from the empirical equation $-\ln(a - x) = 1.8155 + (5.63_3 \times 10^{-6})t + (1.81 \times 10^{-12})t^2$. This equation was obtained from the experimental points of Table I by grouping the first three, the second three and the last five to obtain the three simultaneous equations according to the method of averages mentioned above.

The values of k_1 in Table II were calculated from equation (1) and the two values of k_2' from equations (5) and (6), respectively; equation (6) was written in the form

$$k_2 = \frac{1}{[EtTs]}\left[\left(-\frac{d\ \ln[X^-]}{dt}\right) + \frac{[EtX]}{[X^-]}k_3\right] \quad (14)$$

The value of k_3 used here is 1.0×10^{-6} sec.$^{-1}$ (Table VII).

TABLE I

TYPICAL EXPERIMENTAL RECORD FOR k_1, TIME IN SECONDS

Expt. 85: initial concn. EtTs = 0.1627_6

t, sec.	Acid titer[a]	$[H_3O^+]$	[EtTs]	$k_1 \times 10^6$
0	0	0	0.1627_6	5.63
2230	0.39	0.0020_0	$.1607_6$	5.64
10440	1.81	$.0093_0$	$.1534_6$	5.67
17350	2.96	$.0152_1$	$.1475_5$	5.70
23290	3.92	$.0201_4$	$.1426_2$	5.72
32650	5.36	$.0275_4$	$.1352_2$	5.75
38990	6.31	$.0324_2$	$.1303_4$	5.77
83520	12.10	$.0621_6$	$.1006_0$	5.94
86510	12.53	$.0643_7$	$.0983_9$	5.94
88810	12.77	$.0656_0$	$.0976_1$	5.95
95870	13.50	$.0693_5$	$.0934_1$	5.98
102170	14.16	$.0727_4$	$.0900_2$	6.00

[a] In cc. of 0.02584 *N* NaOH per 5.03_0 cc.

Results

Data for the ethyl toluenesulfonate solvolysis in the solvent only and in the presence of various salts are given in Tables IV and V. These initial specific rates of solvolysis are plotted in Fig. 1 as a function of the initial ester concentration. By comparing Table I with Fig. 1 it may be seen that the values of k_1 during the course of the ester

TABLE II

TYPICAL EXPERIMENTAL RECORD FOR k_1 AND k_2' IN THE PRESENCE OF BROMIDE AND PERCHLORATE, TIME IN SECONDS

Expt. 60: initial concn. EtTs = 0.13410; initial concn. KBr = 0.05373; initial concn. $NaClO_4$ = 0.05352

t, sec.	$[Br^-]$	Interpolated $[H_3O^+]$	$[EtTs]^a$	$-\frac{d \ln (a-x)}{dt} \times 10^6$	$-\frac{d \ln [EtTs]}{dt} \times 10^5$	$-\frac{d \ln [Br^-]}{dt} \times 10^5$	$k_1 \times 10^6$	$k_2' \times 10^4$ Eq. (5)	$k_2' \times 10^4$ Eq. (14)
0	0.05373	0	0.13410	5.355	1.156	1.583	5.360	1.154	1.180
2520	.05172	0.00190	.13019	5.319	1.144	1.536	5.385	1.170	1.183
5510	.04935	.00403	.12569	5.278	1.131	1.481	5.427	1.191	1.185
13500	.04419	.00940	.11516	5.167	1.092	1.331	5.512	1.224	1.175
20410	.04048	.01370	.10715	5.072	1.047	1.225	5.575	1.208	1.174
24480	.03855	.01610	.10282	5.017	1.019	1.183	5.610	1.188	1.189
32830	.03498	.02095	.09440	4.900	0.975	1.117	5.674	(1.166)	(1.240)
37550	.03314	.02350	.09001	4.833	.961	1.083	5.710	(1.177)	(1.272)
42950	.03151	.02630	.08558	4.758	.953		5.733	(1.206)	

[a] It is apparent that $[EtBr]_t = [Br^-]_0 - [Br^-]_t$ and that $[EtTs]_t = [EtTs]_0 - [H_3O^+]_t - [EtBr]_t$.

TABLE III

TYPICAL EXPERIMENTAL RECORD FOR k_2 IN THE PRESENCE OF HYDROXYL ION, TIME IN SECONDS

Expt. 66: initial concn. EtTs = 0.14571; initial concn. NaOH = 0.10895

t, sec.	OH^- titer^a	$[OH^-]$	$[EtTs]$	$k' \times 10^4$	$k'' \times 10^5$	$k_1^b \times 10^6$	$k_2 \times 10^4$ Eq. (9)	$k_2 \times 10^4$ Eq. (10)
0		0.10895	0.14571	3.383	3.636	5.72	2.86	2.81
1080	23.48	.10347	.14023	3.417	3.522	5.76	2.86	2.85
3960	20.51	.09038	.12714	3.525	3.225	5.82	2.88	2.92
11270	15.14	.06672	.10348	3.853	2.567	5.94	2.96	2.96
15840	12.66	.05579	.09255	4.075	2.253	6.00	3.00	2.96
20520	10.64	.04689	.08365	4.305	1.989	6.04	3.02	2.95
25130	9.05	.03988	.07664	4.528	1.789	6.08	3.00	2.96
32650	7.01	.03089	.06765	4.900	1.561	6.12	2.92	3.07

[a] In cc. 0.02221 *N* HCl per 5.040 cc. [b] Read from Fig. 1 for the appropriate [EtTs].

TABLE IV

INITIAL SPECIFIC RATES OF SOLVOLYSIS $(k_1)_0$ IN 60.72% DIOXANE AT 50°, TIME IN SECONDS

Initial concn. EtTs	Added solutes	Added solutes Concn. mole/l.	$(k_1)_0 \times 10^6$
0.02215			6.27
.04402			6.27
.05253	$NaClO_4$	0.10840	6.22
.07610			6.14
.07925			6.05
.07944			6.08
.08248	$NaClO_4$	.10794	5.99
.08793	NaTs	.10766	5.91
.09464			6.07
.09643			6.13
.10437	$NaClO_4$	.10741	5.88
.10611			5.85
.10672			5.85
.10923	$NaClO_4$	.10744	6.01
.10966			5.90
.11814			5.93
.12994			5.73
.13053			5.77
.13642	$NaClO_4$	.10696	5.68
.14597			5.70
.14695	NaTs	.10654	5.61
.15261			5.74
.15567			5.66
.15739	$NaClO_4$	.10643	5.70
.16276			5.63
.18708			5.65

reaction drift upward approximately as one would predict from the changing ester concentration.

Also listed in Table V are the second order displacement constants $(k_2')_0$ for the halide reaction. It is of interest to observe that in the bromide and chloride displacements the specific rate is greater for smaller initial concentrations of either reactant. This effect is probably although not certainly beyond experimental error; it is most pronounced in the chloride displacement, is just

TABLE V

INITIAL SPECIFIC RATES OF SOLVOLYSIS $(k_1)_0$ AND OF DISPLACEMENT BY HALIDE ION $(k_2')_0$ IN 60.72% DIOXANE AT 50°, TIME IN SECONDS

Initial concn. EtTs	Initial concn. halide mole/l.	Initial concn. halide mole/l.	Concn. $NaClO_4$ mole/l.	$(k_1)_0 \times 10^6$	$(k_2')_0 \times 10^4$
0.08983	NaCl	0.10852		5.64	0.458
.11748	NaCl	.10800		5.58	.447
.08959	NaCl	.05430	0.05400	5.61	.542
.11713	NaCl	.05405	.05375	5.52	.492
.08852	KBr	.12496		5.67	1.125
.15796	KBr	.08391		5.42	1.167
.08008	KBr	.10839		5.64	1.175
.13345	KBr	.10742		5.47	1.128
.08030	KBr	.05445	.05412	5.70	1.181
.13410	KBr	.05373	.05352	5.36	1.172
.08548	KI	.10850		5.17	3.555
.12790	KI	.10780		5.21	3.561

detectable in the reaction with bromide ion and does not appear at all in the iodide reaction.

Table VI reports the values of $(k_2)_0$ for the hydroxyl ion displacement. The results here do not support any significant interpretation of a change in $(k_2)_0$ with changing initial concentrations of reactants. An average value of 2.84×10^{-4} l./mole/sec. is probably correct within 1.5%.

TABLE VI

INITIAL SPECIFIC RATE OF DISPLACEMENT BY HYDROXYL ION, $(k_2)_0$ IN 60.72% DIOXANE AT 50°, TIME IN SECONDS

Initial concn. EtTs	Initial concn. NaOH	Concn. NaClO₄	$(k_1)_0{}^a \times 10^6$	$(k_2)_0 \times 10^4$
0.08252	0.10978			(3.055)
.10654	.10910		5.94	2.822
.13550	.10873		5.78	2.875
.14571	.10895		5.75	2.833
.11308	.05450	0.05385	5.89	3.000
.14623	.05346	.05353	5.72	2.639

[a] Interpolated values read from Fig. 1.

In Table VII appear the solvolysis constants $(k_3)_0$ for the ethyl halides. It is of interest here to note that the relative rate constants for ethyl chloride, ethyl bromide and ethyl iodide, respectively, are approximately in the ratio 1:20:21, while the constants for the methyl halides[8] in the same order are in the ratio 1:18:3.5 at 25° and 1:12.1:4.1 at 100°.

TABLE VII

INITIAL SPECIFIC RATES OF ETHYL HALIDE SOLVOLYSIS, $(k_3)_0$, IN 60.72% DIOXANE AT 50°, TIME IN SECONDS

Initial concn. EtX		Added solutes, Concn. mole/l.		$(k_3)_0 \times 10^6$
EtCl	0.10468			0.064
EtCl	.15175			.036
EtCl	.15476			.058
EtBr	.11401			1.029
EtBr	.15149			0.994
EtBr	.15177	NaTs	0.10786	
EtBr	.16201	NaClO₄	.10797	1.015
EtBr	.20664			0.982
EtBr	.22920			.953
EtI	.07207	(EtI from weight buret)		1.090
EtI	.07741	(EtI in sealed bulb)		1.100
EtI	.10142	NaClO₄	0.10841	1.064
EtI	.14325	(EtI in sealed bulb)		1.042
EtI	.15116	(EtI from weight buret)		1.039
EtI	.16982	NaTs	0.10747	

Table VIII lists the data used in the calculation of $(k'_{-2})_0$ from equation (13). While the differences $[X^-] - [H_3O^+]$ on which this calculation is based are very small they are believed to be significant; a careful consideration of all errors involved offers no explanation of the fact that the halide ion concentration increases slightly faster than the oxonium ion concentration, unless there is some reaction between ethyl halide and toluenesulfonate ion. The specific rate of this displacement in the case of both ethyl bromide and ethyl iodide is approximately 7×10^{-7} l./mole/sec. and is probably correct only to an order of magnitude. This makes the equilibrium constants for the displacement of toluenesulfonate ion by bromide or by iodide ion (reaction C) of the order of 10^2.

TABLE VIII

DATA FOR CALCULATION OF $(k'_{-2})_0$, THE SPECIFIC RATE OF DISPLACEMENT OF BROMIDE ION BY TOLUENESULFONATE ION

Expt. 75: initial concn. EtBr = 0.15177; initial concn. NaTs = 0.10786.

t, sec.	$[H_3O^+]$	t, sec.	$[Br^-]$
43020	0.00628	44400	0.00682
76140	.01099	80100	.01197
163910	.02295	167940	.02364
233710	.03141	235620	.03202
302510	.03957	303660	.03972

With two exceptions all experiments in the presence of added salts were run at constant initial ionic strengths. The magnitude of electrolyte effects, if any, was determined by measurements in the presence of sodium perchlorate.

Discussion

The Order of Reactivities of the Various Ethyl Esters.—The specific rates of the displacement of toluenesulfonate ion from ethyl toluenesulfonate by various anions (Reactions (B) and (C)) decrease in the order $I^- > OH^- > Br^- > Cl^-$ and in the ratio of 1:0.8:0.32:0.14. On the other hand, the rates of hydrolysis (Reactions (A) and (D)) of the various ethyl esters decrease in the order EtTs > EtI > EtBr > EtCl and in the ratio 5.5:1.0:0.96:0.048. Finally the order of decreasing thermodynamic stability of the various esters with respect to displacements of the type

$$X^- + EtY \longrightarrow EtX + Y^-$$

is EtOH > EtI > EtCl > EtTs with a very slight uncertainty with regard to the last two. The results of the present paper show that the toluenesulfonate is less stable than either the bromide or the iodide; it is almost certainly less stable than the chloride. Iodide ion has been found to displace chloride ion almost completely from alkyl chlorides in both acetone and alcohol solutions[9]

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[8] Moelwyn-Hughes, *Proc. Roy. Soc.* (London), **A164**, 295 (1938).

[9] (a) Finkelstein, *Ber.*, **43**, 1528 (1910); (b) Conant and Kirner, THIS JOURNAL, **46**, 233 (1924); (c) Conant and Hussey, *ibid.*, **47**, 476 (1925); (d) Bergmann, Polanyi and Szabo, *Trans. Faraday Soc.*, **32**, 843 (1936).

even when all salts concerned are soluble and there is no displacement of equilibrium due to solubility factors, and the effect is almost certainly general. The position of bromide in this sequence is uncertain. The equilibrium constant for the displacement of bromide ion from methyl bromide by iodide is considerably greater than unity both in aqueous and in methyl alcohol solutions.[8,10] On the other hand, the constant for the displacement of chloride ion from chlorosuccinic acid in aqueous solution by bromide ion is 0.2.[11]

These effects are not isolated or peculiar to the toluenesulfonates or the ethyl esters; the contrast between the order of the thermodynamic stabilities of the halide esters and the order of their reactivities is well known[12]; it is also known that iodide ion may displace chloride ion from an alkyl halide faster than chloride ion does,[9d] and that bromide ion may displace chloride ion faster than chloride ion does.[11] These phenomena have both theoretical and practical interest.

From available thermochemical data[13] and the electron affinities of the halogens[13] the heat content changes for the reactions

$$CH_3Cl + Br^- \longrightarrow CH_3Br + Cl^- \qquad (E)$$

and

$$CH_3Cl + I^- \longrightarrow CH_3I + Cl^- \qquad (F)$$

are 8.3 and 14.9 kcal., respectively. Even with the largest possible allowance for entropy effects the equilibrium constants must be very small numbers of the order of 10^{-6} and 10^{-11} whereas the observed constant is considerably greater than unity for reaction (F) and is not far from unity for reaction (E). Consideration of the energies of solvation of the gaseous ions goes far to resolve the difficulty. Using the values listed by Rice[13] the heats of reaction in aqueous solution become 1.9 and 0.4 kcal., and correcting for the entropies of solution the free energies become 3.0 and 2.5 kcal. Admitting the uncertainty of this calculation, and of the data used and the omission of important factors such as the solvation energy of the alkyl halides, it is still easy to see that a large positive free energy change in the gaseous state may be converted to a small positive change or even to a negative one in solution. Obviously the much greater solvation energy of the smaller ion approximately compensates for the greater energy of its linkage to carbon.

This being the case, the contrast discussed above becomes intelligible if one admits that the halide ions are relatively unsolvated in the transition state of the various reactions under consideration. In the reaction

$$X^- + EtTs \longrightarrow [X—Et—Ts]^- \longrightarrow XEt + Ts^-$$

the solvation energy must be supplied in the formation of the transition state, and the order of the reactivities is therefore that of the thermodynamic stabilities in solution. In the reaction

$$EtX \longrightarrow Et—X \longrightarrow EtOH + X^- + H^+$$

relatively little solvation energy is involved, the effects of the bond energies predominate, and the order of reactivity is that of the thermodynamic stability in the gaseous state.

TABLE IX

PERCENTAGE CHANGE IN SPECIFIC RATE OF SOLVOLYSIS OF 0.1 *M* EtTs ON ADDITION OF THE VARIOUS SOLUTES AT 0.108 *M* CONCENTRATION

Solute	% change in sp. rate
EtTs	− 8.5
NaClO$_4$	0
NaTs	− 2.3
NaCl	− 6.0
KBr	− 6.0
KI	−12.5

The Detailed Kinetics of the Reactions.— These reactions show both resemblances and differences when compared with the analogous reactions of benzyl chloride in the same solvent mixture.[4] Figure 1 and Table IX show the effect of various solutes upon the specific rate $(k_1)_0$ of the hydrolysis of ethyl toluenesulfonate (reaction (A)). Increasing the concentration of the ester decreases the specific rate as it does with benzyl chloride, in this case by 14% when the ester concentration changes from 0.02 *M* to 0.18 *M*. In contrast to the benzyl chloride case sodium perchlorate does not change the rate appreciably; consequently there seems to be no salt effect attributable to the ionic atmosphere of an electrolyte. Sodium toluenesulfonate also has very little effect, which means that a "common ion effect" such as that produced by chloride ion in the solvolysis of benzyl chloride[4] and various derivatives of benzhydryl chloride[14] is absent. Constants measured in the presence of halide ions show, however, a significant decrease

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[10] Moelwyn-Hughes, *Trans.* Faraday *Soc.*, **35**, 368 (1939).

[11] Olson and Long, THIS JOURNAL, **56**, 1294 (1934).

[12] Hammett, ref. 2, p. 156 (refs.).

[13] Rice, "Electronic Structure and Chemical Binding," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

[14] (a) Church, Hughes, Ingold and Taher, *J. Chem. Soc.*, 971 (1940); (b) Bateman, Hughes and Ingold, *ibid.*, 974 (1940).

in the specific rate of the solvolysis. The magnitude of the effect is practically the same in the chloride and bromide cases, while the decrease in the presence of potassium iodide is quite a bit greater. The effect would appear to be of the same nature as that exerted by acetate ion upon the rate of production of benzyl alcohol from benzyl chloride[4] or that exerted by azide ion upon the rate of production of dimethylbenzhydrol from dimethylbenzhydryl chloride[14b] and to indicate that some at least of the hydrolysis goes by way of the ionic mechanism

$$EtTs \longrightarrow Et^+ + Ts^-$$
$$Et^+ + 2H_2O \longrightarrow EtOH + OH_3^+$$

If the halide ion diverts part of the ethyl ion to the formation of ethyl halide

$$Et^+ + X^- \longrightarrow EtX$$

the total rate of formation of alcohol and of titratable acidity must decrease.

During the course of a hydrolysis the specific rate k_1 (see Table I) increases about as one would predict from the change in concentration of ethyl toluenesulfonate. This is consistent with previous observations[15] to the effect that the hydrolysis of toluenesulfonates is not catalyzed by acids, and indicates further that ethyl alcohol in small amounts has a negligible effect upon the rate of hydrolysis.

The lack of an appreciable general salt effect of the sort which perchlorates exert upon the hydrolysis of benzyl chloride suggests that the transition state in the hydrolysis of ethyl toluenesulfonate is less polar and corresponds to a smaller separation of charges than is the case with benzyl chloride.

Summary

The rates of the solvolytic reactions of ethyl toluenesulfonate and of ethyl chloride, bromide and iodide and the rates of the displacement of toluenesulfonate ion by chloride, bromide, iodide and hydroxyl ions have been measured in a 60.72% dioxane–39.28% water medium at 50°. Iodide ion displaces toluenesulfonate ion from ethyl toluenesulfonate at a greater rate than do the other halide ions; nevertheless, ethyl iodide, of all the ethyl halides, is most rapidly decomposed by hydrolysis. This apparent paradox may be accounted for in terms of the fact that the lower solvation energy of iodide ion approximately compensates for its weaker binding to carbon. The equilibrium constants for the displacement of toluenesulfonate ion by bromide and by iodide ion are of the order of 10^2. Halide ions decrease the rate of formation of ethyl alcohol from ethyl toluenesulfonate, an effect which is consistent with an ionic mechanism of solvolysis.

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[15] Praetorius, *Monatsh.*, **26**, 1 (1905); Wegscheider, *Z. physik. Chem.*, **41**, 52 (1902).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF HAVERFORD COLLEGE AND THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING OF THE UNIVERSITY OF PENNSYLVANIA]

Transition Phenomena Involving Decahydrated Mixed Crystals of Sodium Sulfate and Sodium Chromate[1]

BY WILLIAM E. CADBURY, JR.,[2] WILLIAM B. MELDRUM AND WALTER W. LUCASSE

The temperature of transition of sodium sulfate decahydrate into the anhydrous form is 32.383° on the International Hydrogen Scale,[3] while that of sodium chromate decahydrate into the hexahydrate is 19.525°, and into the tetrahydrate is 19.987°.[4] It is known that sodium chromate lowers the transition temperature of sodium sulfate decahydrate. Richards and Kelley[4] have reported that sodium sulfate *raises* the temperature of transition of sodium chromate decahydrate into the hexahydrate. They reported an elevation of as much as 4°.

At sufficiently low temperatures sodium sulfate and sodium chromate decahydrates form mixed crystals in all proportions. When these mixed crystals are warmed they undergo transition, losing water of crystallization and forming another solid phase and a saturated solution. The temperature at which solution and two solid

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[1] Part of the material in this paper was presented before the Philadelphia Meeting of the American Association for the Advancement of Science, December 28, 1940.

[2] This paper is abstracted from part of a dissertation presented by William E. Cadbury, Jr., to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1940.

[3] Richards and Wells, *Proc. Am. Acad. Arts Sci.*, **38**, 43 (1902); *Z. physik. Chem.*, **43**, 465 (1903).

[4] Richards and Kelley, THIS JOURNAL, **33**, 847 (1911).