given in the tables. This maximum thus varied in such a way as to indicate that it was not an equilibrium. Furthermore, it occurred at a dilution far too low for the soap to be in colloidal form. This sharp peak of effect occurred over a very narrow range and rapidly fell off to zero on still greater dilution.

Since a very minute absolute amount of suspension would be sufficient to cause a large effect relative to the soap in this dilution, the following experiments were devised to eliminate suspension of solid dye by avoiding the presence of any solid dye. A saturated solution of dye was prepared in hexadecane and then excess hexadecane was added to reduce the concentration to 90% of saturation. Hexadecane is a hydrocarbon which is not itself solubilized in dilute potassium laurate. Two cc. of this solution was placed on top of 20 cc. of the dilute soap solution containing salt. These were then placed on a rotating plate in a thermostat at 25° in such a manner that the interface between soap and hydrocarbon was not broken, but the liquids were kept very gently stirred. After a week of such treatment the aqueous soap layer was removed, and the concentration of dye in it was measured. The maxima had entirely disappeared, showing that those observed with solid dye were due to suspension of residual fine fragments from dye crystals. These would be too small to play any role in comparison with the very much larger amounts of soap in greater concentrations.

Solubilization of a Non-electrolytic Detergent with and without Added Salt.—It is of great interest to compare the behavior of a non-electrolytic detergent such as X with that of the colloidal electrolytes so far investigated. X is an alkylated aryl poly ether alcohol derived from polymerized ethylene oxide and it cannot ionize in aqueous solution. Hence there can be no common ion effect. Nevertheless addition of salt in general might be expected to promote association. Measurements of the solubilization of Orange OT in 2% solution of X alone at 25° gave 9.25 mg./100 cc. Addition of 10% potassium chloride raised this to 11.15 mg./100 cc., a result 20% greater. This is almost half as great an effect in increasing solubilization as if the salt had been added to a colloidal electrolyte such as potassium laurate This may be taken as an indication that non-electrolytic detergents are associated in aqueous solution.

Summary

The solubilization of water-insoluble dyes has been measured in aqueous solutions of soaps at 25°. Whereas the amount of hydrocarbon chain in the molecule of soap or in the soap micelle increases from the caprylate to the myristate only in the proportion 1:1.25:1.50:1.75, the solubilization increases disproportionately as 1:2.14:6.48:11.61. In all concentrations of potassium laurate above $N/1000$ the addition of potassium hydroxide or of potassium salts greatly increases the amount of solubilization. This solubilization occurs at dilutions of soap far below those in which soap alone can be solubilized, owing to the absence of colloidal micelles, but it increases rapidly and steadily with increasing concentration of soap showing that the kinds of micelles existing in higher concentrations are more effective than those formed in lower concentrations.

Extremely dilute soap solutions, especially in the presence of salt, exhibit a powerful suspending action for any minute particles of dye, a phenomenon quite distinct from solubilization.

Solubilization by a non-electrolytic detergent is also enhanced by the presence of potassium chloride, indicating increased association of the detergent.

STANFORD UNIVERSITY, CALIF. RECEIVED MARCH 22, 1946

The Kinetics of the Reaction of Hydroxyl Ion with the Meso and Racemic Di-*p*-toluenesulfonates of Butylene Glycol-2,3[1]

BY FREDERICK C. FOSTER[1a] AND LOUIS P. HAMMETT

The substitution of methyl for hydrogen has an effect upon the reactivity of alkyl halides, toluenesulfonates, and the like which is consistent and well-known. For nucleophilic displacements such

$$Y + R_3CX \longrightarrow R_3CY + X \qquad (1)$$

as the reactions with hydroxyl, halide, or acetate ions or with ammonia and amines, the rate of reaction drops rapidly in the series CH_3, CH_3CH_2-, $(CH_3)_2CH$- $(CH_3)_3C$-.[2] For the kinetically first order solvolytic reactions and the reactions with silver ion and the like, the rate of reaction increases in the same order.[2] A less thoroughly explored series is offered by the substitution of —CH_2X for hydrogen, where X is hydroxyl, toluenesulfonate, halogen, or similar substituents. This has particular practical interest in the reactions of the sugar toluenesulfonates, where a distinction is frequently drawn between "primary" and "secondary" groups, *i. e.*, between the first

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[1] Dissertation submitted by Frederick C. Foster in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science Columbia University.

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[2] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 152–155.

and second groups in CH$_2$OTs-CHOTs-CHOTs-. The analogy to ordinary primary and secondary alcohol derivatives implied by the nomenclature has some justification in the fact that the rate of reaction of "primary" toluenesulfonate groups in nucleophilic displacements, such as the reactions with iodide or hydroxyl ions, is indeed materially greater than that of "secondary" groups. The difference is large enough and appears to be consistent enough to permit the development of various diagnostic and preparative procedures.[3]

In the effort to obtain further information on this effect we first investigated the reactions of ethylene glycol di-*p*-toluenesulfonate, which turned out to be unexpectedly complicated. In a dioxane–water medium, containing 60.72% dioxane by weight, reaction at 50° gave rise to much aldehyde, whether in the solvolytic reaction or in the nucleophilic reaction with hydroxyl ion. The presence of aldehyde was first suspected from the development of an orange color in the alkaline reaction mixtures, presumably due to aldehyde resins. It was confirmed by subsequent tests with Schiff reagent, with hydroxylamine, with bisulfite, and with ferricyanide. None of these reagents, however proved reliable for the quantitative estimation of the amount of aldehyde produced and attempts at detailed kinetic study of the reactions of the ethylene glycol derivative were therefore abandoned. In view of the general similarity of the reactions of toluenesulfonates to those of alkyl halides, the aldehyde formation in this case is no doubt comparable to the appearance of aldehyde in the hydrolysis products of ethylene bromide and ethylene chloride.[1]

The complication of aldehyde formation in these reactions introduces an error of unknown magnitude in the kinetic measurements, and permits in fact only an estimation of the upper limit of the specific rate of the hydrolysis reactions. Even this, however, is sufficient to demonstrate that in the kinetically first order solvolysis the glycol is at most one-twentieth as reactive as ethyl toluenesulfonate. For the latter accurate measurements[5] in the same medium and at the same temperature as in the present work give a half life of thirty hours, while the present results give a half life for the glycol ester of at least 640 hours. In view of the competing reactions and the possible statistical effect in the glycol case, the reactivity of the ester group in the glycol ester with respect to solvolysis must be less than that in the ethyl ester by at least the inverse ratio of these numbers. With respect to the second order displacement of toluenesulfonate ion by hydroxyl ion, the uncertainties in the glycol case make any comparison of reactivities with the ethyl ester meaningless. Our data on the ethylene-glycol toluenesulfonate permit therefore one but only one qualitative conclusion, namely, that *in the solvolytic reaction* substitution of —OTs for hydrogen on the beta carbon atom decreases the reactivity by a large factor. It may or may not be coincidence that the effect is in the same direction as that produced by the substitution of methyl for hydrogen on the same (the beta) carbon atom.[2]

Because of this difficulty with the ethylene glycol ester, we turned to the di-*p*-toluenesulfonate of butylene glycol-2,3, which we found to be free from the complication of aldehyde or ketone formation. Here there is an interesting further variable of stereoisomerism; consequently both racemic and meso esters were isolated and studied kinetically.

All kinetic measurements were made in a dioxane–water medium containing 60.72% dioxane by weight.

Synthetic Part

Four hundred cc. of diacetyl (Forest Products Chemical Co., Memphis, Tennessee) was hydrogenated at high pressure with Raney nickel as catalyst at a temperature of 110°. The resultant glycol was dried by adding benzene and distilling off the hetero-azeotrope of benzene and water. The glycol was finally distilled at 2 mm. pressure at a temperature of 58°. The temperature of the distilling flask should not be allowed to exceed 100°, because decomposition occurs at higher temperatures. The yield of butylene glycol-2,3 was 317 cc.

To 85 cc. of the mixture of *meso* and racemic butylene glycol-2,3 was added 490 g. of "practical" grade *p*-toluenesulfonyl chloride and 400 cc. of pyridine. The reaction mixture was kept in an ice-bath for three hours and then allowed to come slowly to room temperature by standing overnight. The reaction mixture was then diluted with chloroform and ice water. The water layer was separated and extracted three times with chloroform. The chloroform solutions were then washed several times with dilute sulfuric acid, water, dilute sodium carbonate and finally water, taking precautions to keep the solutions cold. After drying with anhydrous sodium sulfate, the solvent was removed and the tosyl esters precipitated with ethyl alcohol. The yield of crude tosyl esters was 250 g.

Several solvents were tried in order to find a method of separating the two tosyl esters by fractional crystallization. In all cases except one, the recrystallized product melted at 70–80°, which was the same melting range as the crude tosyl esters. However, after one recrystallization from ether the melting point of the crystals rose to 89.5–92.5°. The successive melting points were 94–95, 96, 96, 96°. This ester was later proved to be the *meso* ester.

The *meso* and racemic di-*p*-toluenesulfonates of butylene glycol-2,3 may each be isolated by fractional crystallization of the mixture of esters from ether. For obvious reasons, yield was sacrificed for purity and 250 g. of the crude tosyl esters yielded 45 g. of *meso* ester.

Anal. Calcd. for C$_{18}$H$_{22}$O$_6$S$_2$: C, 54.25; H, 5.57. Found: C, 54.46; H, 5.65.

Since the racemic ester is the more soluble in ether, it is difficult to obtain it pure by fractional crystallization. In order to synthesize and identify the racemic ester the mixed diacetates of butylene glycol-2,3 were therefore prepared by the method of Wilson and Lucas.[6]

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[3] J. W. H. Oldham and J. K. Rutherford, THIS JOURNAL, **54**, 366 (1932); P. A. Levene and A. L. Raymond, *J. Biol. Chem.*, **102**, 317 (1933); F. B. Cramer and C. B. Purves, THIS JOURNAL, **61**, 3458 (1939).

[4] A. Lieben, *Monatsh.*, **23**, 60–75 (1902); L. Carius, *Ann.*, **131**, 173 (1864); H. Bahr and H. Zieler, *Z. angew. Chem.*, **43**, 286–289 (1930).

[5] H. R. McCleary and L. P. Hammett, THIS JOURNAL, **63**, 2254 (1941).

[6] C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2401 (1936).

The racemic diacetate was isolated from the mixture by recrystallizing several times from petroleum ether. Its melting point was 44°, as compared to 41.0–41.5° reported by Wilson and Lucas.[6]

Using the method described by Isbell,[7] the racemic diacetate of butylene glycol-2,3 was hydrolyzed catalytically by barium methylate in absolute methyl alcohol. Eleven grams of racemic glycol was obtained from 40 g. of racemic diacetate.

Tosylation of the racemic butylene glycol-2,3 was carried out in the same manner as the tosylation of the mixture of glycols described previously. Eleven grams of racemic glycol yielded 35 g. of racemic di-*p*-toluenesulfonate of butylene glycol-2,3, m. p. 82°.

Anal. Calcd. for $C_{18}H_{22}O_6S_2$: C, 54.25; H, 5.57. Found: C, 54.37; H, 5.46.

As a criterion of purity, both the racemic and *meso* di-*p*-toluenesulfonates of butylene glycol-2,3 were recrystallized at least three times to a constant melting point. One of these recrystallizations for the *meso* ester was performed in a different solvent from the other re-crystallizations.

The proof that the lower melting tosyl ester is the racemic ester is based on the fact that it was prepared from the racemic diacetate, a known compound. The carbon–oxygen bonds were not broken in the two reactions which linked the diacetate to the ditosyl ester, so there was no opportunity for inversion.

The racemic ditosyl ester which was isolated as the more soluble ester after the fifth stage of fractional crystallization had a melting point three degrees below that of the pure racemic ester. Because there was obviously a trace of the *meso* ester present, this material was not used in any of the kinetic measurements.

Di-*p*-toluenesulfonate of Ethylene Glycol.—Ethylene glycol was tosylated by the method of Butler and Nelson,[8] the melting point, 126°, checked theirs.[8]

Anal. Calcd. for $C_{16}H_{18}O_6S_2$: C, 51.89; H, 4.86. Found: C, 51.97; H, 4.80.

Kinetic Part

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

Materials.—1,4-Dioxane (Carbide and Carbon Chem. Co.) was purified in 2–3 liter quantities as described by Beste and Hammett.[9]

Solutions of reaction mixtures, in which both sodium perchlorate and sodium hydroxide were present, were prepared by adding a carbon dioxide-free sodium hydroxide solution to a solution of Mallinckrodt A.C.S. grade perchloric acid.

Method.—Due to the slowness of the reactions and the low concentration of ester which was necessitated by solubility considerations, the kinetic experiments could not be made in glass apparatus. Preliminary runs in soft glass ampoules showed that the sodium hydroxide reacted about one-third as fast with the glass as it did with the ester at the concentrations of the present experiments.

In Pyrex glass ampoules the results were even less favorable. The reaction mixture split into two phases after a short time. The new liquid phase was less than 1 cc. and settled at the bottom of the ampoules. It is probable that this phenomenon was caused by the reaction of the sodium hydroxide with the boron trioxide in the Pyrex glass and that the resultant salt caused a gradual salting out of the dioxane. In fact a few crystals of borax added to a freshly prepared reaction mixture caused a similar effect.

Four of the kinetic experiments were made in soft glass ampoules containing six coats of silver precipitated by a reducing sugar in the usual manner. These silvered ampoules were successful in following the reaction to about 30% completion, or about fifty hours. After this time, the sodium hydroxide began to attack the glass and irregular results were obtained.

The remaining kinetic experiments were made in stainless steel bottles. A disk of stiff cardboard and a disk of silver-plated copper sheeting served as gaskets inside the stainless steel caps to make the reaction bottles leak-proof.

It was found that it was necessary to flush the reagent bottles with nitrogen before the start of the reaction and each time a sample was removed. The decomposition of the dioxane by the oxygen of the air over such a long period caused a small error by decreasing the basicity of the reaction mixture.

The reaction mixtures were made up by weighing all of the components. First the ester was weighed and transferred to a glass bottle. The dioxane was next weighed into the bottle and solution of the ester accomplished. Finally, the aqueous solution of sodium hydroxide, or of sodium hydroxide plus sodium perchlorate, was added. After agitation, the solution was transferred to a stainless steel bottle and an initial sample removed. The steel bottle was then flushed with nitrogen and placed in the thermostat. Since the reactions were slow and were carried out at 60°, the amount of reaction which occurred before the insertion of the reaction mixtures in the thermostat was negligible.

To remove a sample, the stainless steel bottle was taken from the thermostat and placed in a large water-bath which was run at room temperature. When the bottle had attained room temperature, it was shaken well and a sample for analysis withdrawn, transferred to an excess of standard hydrochloric acid solution, and titrated with standard base using brom cresol purple as indicator. The reaction bottle was flushed with nitrogen before replacement in the thermostat.

In order to express the concentrations in the conventional moles per liter, density measurements were made on the reaction mixtures. Since all samples of reaction mixtures were removed at room temperature, the density measurements were also made at room temperature. In all reaction mixtures, the ratios of the densities at room temperature to the densities at 60° ranged from 1.028 to 1.031. Initial concentrations and all titers were calculated on the basis of the reaction mixtures at room temperature.

Solvolytic and Acid Reaction.—Preliminary runs were made on the solvolytic hydrolysis and the acid hydrolysis in the presence of 0.4 molar perchloric acid of the esters. These runs were carried out in glass ampoules flushed with nitrogen with an initial concentration of ester of 0.026 molar. After a month at 60°, reaction had proceeded to only about one-tenth of completion. Within experimental error, there was no difference between the rates of the solvolytic and acid reactions.

Tests for Aldehyde and Ketone.—A reaction mixture prepared from 0.026 molar mixed ditosyl esters (*meso* and racemic) of butylene-glycol and 0.14 molar sodium hydroxide in 70% dioxane was allowed to react until the ester was 97.5% hydrolyzed, and the solution was then tested for methyl ethyl ketone by the nitroprusside test.[10] The test was negative, whereas the limiting sensitivity of the test on known methyl ethyl ketone solutions was found to lie between 0.0012 and 0.012%. Consequently no more than 6% of the glycol tosylate could have been converted to the ketone.

An identical reaction mixture was tested for aldehyde with Schiff reagent.[11] Again the test was negative, while the limiting sensitivity was found to lie between 0.0002 and 0.002 molar acetaldehyde. This indicates that no more than 9% of the glycol tosylate could have been converted to aldehyde. The complete absence of aldehyde resin color in the alkaline reaction mixtures confirms the conclusion that little if any aldehyde is formed in this system.

Rate Calculations.—The following abbreviations will be used in this section: a is initial concentration of di-ester, b initial concentration

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(7) H. S. Isbell, *Bur. Standards J. Research*, **5**, 1185 (1930).

(8) Butler, Nelson, Renfrew and Cretcher, This Journal, **57**, 575 (1935).

(9) Beste and Hammett, *ibid.*, **62**, 2481 (1940).

(10) Snell, "Colorimetric Methods of Analysis," Vol. II, D. Van Nostrand Co., Inc., New York, N. Y., 1936, p. 100.

(11) Ref. 10, p. 61.

of hydroxyl ion, x concentration of *p*-toluenesulfonate ion at time t, t time in seconds.

With only the above quantities known, it is impossible to integrate the equation for a consecutive bimolecular reaction.[12] In order to calculate the rate constants of the reactions studied, the pseudo-unimolecular reaction was first examined. Specifically it was considered that in the reaction of 0.22 molar sodium hydroxide with 0.012 molar ester the concentration of base remains effectively constant throughout the reaction because it is so much larger than the initial concentration of ester.

The integrated equation for two consecutive first order reactions is the expression

$$x = a\left[\frac{1}{r-1}e^{-rk_1't} + \frac{1-2r}{r-1}e^{-k_1't}\right] + 2a \qquad (2)$$

where k_1' equals the first order rate constant for the first step, k_2' equals the corresponding constant for the second step and r equals k_2'/k_1'.

The constants may be evaluated by the method of Pedersen.[13] Values of r are selected at random. For each value of r, a value of k_1 may be calculated for each set of experimentally determined values of x and t. The value of r, for which the variation of k_1 is smallest, may be determined either graphically or by observation.

Application of this method to the experimental data showed that the equation (2) is best satisfied for all the experimental pairs of x and t by $r = {}^1/_2$ or $r = \infty$.

If $r = {}^1/_2$, equation (2) becomes

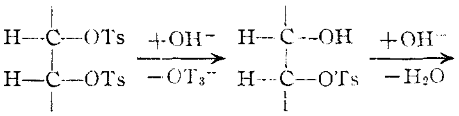
$$2.303 \log_{10} \frac{a}{a - {}^1/_2 x} = \frac{1}{2} k_1't \qquad (3)$$

If $r = \infty$, equation (2) becomes

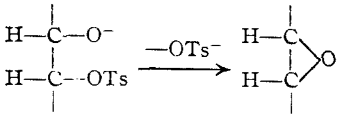
$$2.303 \log_{10} \frac{a}{a - {}^1/_2 x} = k_1't \qquad (4)$$

Since these equations differ only by a factor of 2, no choice can be made between the two values of r from the kinetic data.

It has been reported[8,14] that monoesters of glycols including ethyleneglycol monotosylate disproportionate rapidly to glycol and diester. It has also been found[15] that compounds of the type —CHOTs—CHOTs— yield the epoxides on hydrolysis. The reaction is probably analogous to the formation of epoxides from the alkaline hydrolysis of chlorohydrins and probably has a similar mechanism[16]



$$\begin{array}{c} | \\ H—C—OTs \\ | \\ H—C—OTs \\ | \end{array} \xrightarrow[-OT_3^-]{+OH^-} \begin{array}{c} | \\ H—C—OH \\ | \\ H—C—OTs \\ | \end{array} \xrightarrow[-H_2O]{+OH^-}$$



(5)

If the last step is fast, the value of r in equation (2) would be infinity. The analogous reaction of ethylene chlorohydrin with hydroxyl ion to form ethylene oxide[17] is indeed several orders of magnitude faster than the hydrolysis reactions here reported, and the reaction of the monotosylate should be faster than that of the chlorohydrin.

The value of r would be expected to be one-half if the reaction is an uncomplicated two-step hydrolysis and if the probability of reaction is the same for each ester linkage in both diester and monoester. . The value of one-half has indeed been observed in the acid hydrolysis of ethyleneglycol diacetate[18] and in symmetrical esters of dibasic acids. On the whole, however, the value of ∞ seems the more probable for the glycol tosylate and is used in our calculations.

In the case where $r = \infty$, the full equation for the rate-determining step of the hydrolysis of diester is

$$\mathrm{d}y/\mathrm{d}t = k_1[a - y][b - 2y] \qquad (6)$$

where y is the concentration of diester which has reacted at time t.

Integration of equation (6) yields

$$\log_{10} \frac{b - 2y}{a - y} = \frac{b - 2a}{2.303} k_1t + \log_{10} \frac{b}{a} \qquad (7)$$

or, since in this case $y = {}^1/_2 x$

$$\log_{10} \frac{b - x}{a - x/2} = \frac{b - 2a}{2.303} k_1t + \log_{10} \frac{b}{a} \qquad (8)$$

Equation (8) was used to calculate all values of k_1.

Results

The experimental results of this investigation are given in Tables I and II. Twelve of the kinetic experiments were followed past the half-life of the reaction. The remaining experiments were followed to an average of 40% completion.

In all cases, k_1 drifted downward during the course of the reaction. This drift was not greatly beyond experimental error. Since it occurred in every determination, it must be accepted as real. Because of the observed drift of k_1, all specific rates listed in Table I are average values for the same period of the reaction (to 30% completion).

From the data listed in Table I it may be observed that the variation of the concentrations of ester and base is extremely limited. Higher concentrations of base would have produced a heterogeneous system by "salting-out" the dioxane. Extending the base concentrations to lower values would have the disadvantage of requiring weeks to follow a reaction. Because of

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[12] J. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, New York, N. Y., 1929, pp. 436, 437.

[13] Pedersen, *J. Phys. Chem.*, **37**, 754 (1933).

[14] E. Fischer, *Ber.*, **53**, 1634 (1920).

[15] G. J. Robertson and J. W. H. Oldham, *Nature*, **133**, 871 (1934); D. S. Mathers and G. J. Robertson, *J. Chem. Soc.*, 1076 (1933).

[16] S. Winstein and H. J. Lucas, THIS JOURNAL, **61**, 1577 (1939).

[17] L. Smith, *Z. physik. Chem.*, **A152**, 153–156 (1931); L. O. Winstrom and J. C. Warner, THIS JOURNAL, **61**, 1205–1210 (1930).

[18] J. Meyer, *Z. physik. Chem.*, **66**, 81 (1909); see also C. K. Ingold, *J. Chem. Soc.*, 133, 1375 (1930).

TABLE I

VALUES OF $k_1 \times 10^5$ (LIT. MOLE^{-1}, SEC.$^{-1}$) FOR THE *meso* AND RACEMIC DI-TOSYL ESTERS OF BUTYLENEGLYCOL-2,3

60°

Ester =	0.01234		0.01950		0.02650		0.02650		0.02650	
NaOH =	0.2200		0.2200		0.2200		0.1572		0.1070	
$NaClO_4$ =							0.0628		0.1130	
	Racemic	Meso	Racemic	Meso	Racemic	Meso	Racemic	Meso	Racemic	Meso
	1.26	0.90	1.21	0.90	1.14	0.91	1.23	0.95	1.38	1.09
	1.17	.91	1.13	0.93	1.18	.84	1.20	.98	1.37	1.07
	1.19	.89				.83		.99	1.36	
	1.20	.93								
	1.10	.92								
	1.18	.94								
Average Values	1.18	0.91	1.17	0.91	1.16	0.86	1.22	0.97	1.37	1.08

80°

Ester = 0.01234
NaOH = 0.2200

Meso	Racemic
7.8	8.8
7.4	8.3
7.8	8.3
7.0	8.6
6.2	9.1
Average Values	
7.2	8.6

solubility requirements, the ester concentration could not exceed the low values of the present experiments.

In twelve of the experiments, the initial concentrations of hydroxyl ion did not coincide with the standard values listed in Table I. The values of the specific rates for these experiments were calculated back to the standard concentration values by correcting for the variation of specific rate with initial concentration of hydroxyl ion. This correction never amounted to more than 4%. The values of the rate constants thus obtained were averaged with the constants of the standard concentration runs.

TABLE II

SAMPLE DATA: REACTION OF HYDROXYL ION WITH THE MESO DI-*p*-TOLUENESULFONATE OF BUTYLENE GLYCOL-2,3 AT 60°

Initial Concentration of Meso ester = 0.02649

t, sec.	Titer[a]	OH^-	Ester	$k_1 \times 10^5$
0	4.55	0.1572	0.02649	
13,260	5.79	.1561	.02593	1.03
52,560	9.19	.1531	.02440	1.01
86,040	11.79	.1507	.02323	0.99
125,100	14.77	.1480	.02189	1.00
203,700	19.49	.1438	.01976	0.96
222,240	20.75	.1427	.01920	.97
286,140	23.76	.1400	.01784	.93
355,500	26.34	.1376	.01668	.89

[a] In cc. of 0.02251 N sodium hydroxide per 24.99_2 cc.

Precision.—Errors due to sampling reaction mixture and pipetting the acid to which it is transferred are estimated to lead to an uncertainty of between 3 and 4% in the value of k, and other measurement errors should be unimportant in comparison. The reproducibility of the values reported in Table I is consistent with this estimate.

Discussion

From the heats of activation found, the rates of the displacement of toluenesulfonate by hydroxyl ion at 50° corrected for the statistical effect are computed as 3.5×10^{-6} for the *meso* and 4.6×10^{-6} for the racemic ester.[19] These are less, by factors of 0.0125 and 0.0164, respectively, than the values found for the corresponding reaction of ethyl *p*-toluenesulfonate under the same conditions. In the second order nucleophilic displacement, therefore, the substitution of the group —CHOTs—CH_3 for hydrogen on the alpha carbon produces a large decrease in rate. The effect is in the same direction as that produced by the substitution of alkyl for hydrogen on the same carbon, and is consistent with the previously mentioned difference in reactivity between "primary" and "secondary" toluenesulfonates in the sugar series.

The parallelism with alkyl substitution fails, however, when the solvolytic reaction is considered. Here also the substitution of —CHOTs

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(19) In this instance only, the values of specific rate are those obtained using the value of $r = 1/2$ for the ratio of the second step of the hydrolysis to the first step. This choice of $r = 1/2$ was made only for the purpose of severity in the comparisons of reactivity, since this interpretation yields the larger values for the less reactive butylene glycol esters.

—CH_3 for hydrogen decreases the rate materially.[20] By contrast the reactions of the alkyl halides show an exactly opposite effect, an increase in rate, when alkyl is substituted for hydrogen on the alpha carbon. This result emphasizes further the necessity of caution in transferring a generalization about the effect of substituents on reactivity from one reaction to another of essentially different type and mechanism. The parallelism between the "primary" and "secondary" sugar toluenesulfonates and ordinary primary and secondary alcohol derivatives is valid for nucleophilic displacement reactions; it fails completely for reactions of the solvolytic type.

The specific rate of the hydroxyl ion displacement reaction of the racemic di-*p*-toluenesulfonate of butylene glycol-2,3 at 60° is 1.3 times that of the corresponding meso ester.

Both reactions exhibit a change in specific rate with a change in initial concentration of hydroxyl ion. Increasing the concentration of hydroxyl ion decreases the specific rate, in these reactions by 20% when the hydroxyl ion concentration changes from 0.107 to 0.220 molar. It is interesting to note that no such change of specific rate with initial concentration of hydroxyl ion was observed in the hydroxyl ion displacement reaction on ethyl *p*-toluenesulfonate.[5] Such a phenomenon has been observed, however, in similar reactions. The hydroxyl ion displacement reaction on benzyl chloride[9] showed such a change, but of a smaller magnitude.

The results do not justify any significant interpretation of a change in specific rate with changing initial concentration of ester. However, it should be pointed out again that the range of ester concentrations was exceedingly small due to solubility considerations. Of the two hydroxyl ion displacement reactions mentioned above,[5,9] the benzyl chloride reaction exhibited the "dilution effect" while the ethyl *p*-toluenesulfonate reaction did not. However, a decrease in specific rate with increasing ester concentration of the magnitude exhibited by benzyl chloride over the small range covered in the present experiments would not have been greater than the experimental error.

From a consideration of the above evidence, it can be seen that dilution effects should not cause an observable drift of the specific rate within the experiments. The hydroxyl ion, which exhibits a dilution effect, does not undergo an appreciable change in concentration in the experiments. The observed drift, which is in the opposite direction, must occur from some other source. This drift of the specific rate is probably caused by the increase in the concentration of reaction products during the reaction, producing a change in the medium. Such a phenomenon is common and has been observed in similar reactions.[9]

There is a great deal of evidence[21] demonstrating that the energies of activation of most second order displacement reactions in solution are closely grouped about the value of 20,000. The energies of activation of the two reactions studied are also close to this value. The values of energy of activation, calculated from the Arrhenius equation, are 24,100 and 23,200 for the *meso* and racemic esters, respectively. Since the difference in the calculated values of energy of activation is of the same order of magnitude as the probable error in its calculation, the difference in energies of activation is not significant.

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Summary

The *meso* and racemic di-*p*-toluenesulfonates of butylene glycol-2,3 have been synthesized and identified. The rates of the hydroxyl-ion displacement reactions of these esters have been measured in a 60.72% dioxane–39.28% water medium at 60 and 80°. The specific rates of both reactions vary with the initial concentrations of hydroxyl ion. A comparison of the reactivities of these esters with that of ethyl *p*-toluenesulfonate shows that the substitution of the group —$CHOTs-CH_3$ for hydrogen on the alpha carbon produces a large decrease in the rate of both the nucleophilic displacement with hydroxyl ion and the solvolytic reaction. In the case of the displacement reaction, this result is in the same direction as the effect of alkyl substitution on the same carbon atom and is consistent with the well-known difference in reactivity between "primary" and "secondary" toluene sulfonates in the sugar series. In the case of the solvolytic reaction, this result is in an opposite direction to the effect of alkyl substitution on the same carbon atom and emphasizes the necessity of caution in transferring a generalization about the effect of substituents on reactivity from one reaction to another of essentially different type and mechanism.

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(20) As stated in the experimental section, the solvolytic reactions of the butylene glycol di-esters were found to be exceedingly slow. Four reaction mixtures, including two with 0.4 molar acid added, were prepared with 0.026 molar ester. Within experimental error, these reactions were found to have a one-tenth life of a month at 60°. The ethyl *p*-toluenesulfonate ester has a one-tenth life of five hours at 50° in the same medium. Even if all of the change in titer in the butylene glycol ester reaction be attributed to the first step of the hydrolysis, the tosyl group is about 300 times more reactive in the case of ethyl *p*-toluenesulfonate.

(21) Moelwyn-Hughes, *Chem. Rev.*, **10**, 241 (1932); Moelwyn-Hughes, *J. Chem. Soc.*, 779–784 (1938); Eagle and Warner, THIS JOURNAL, **61**, 488 (1939); Ogg, *Trans. Faraday Soc.*, **31**, 1389 (1935).