nitrate solution using a dichlorofluorescein adsorption indicator according to Kolthoff and collaborators.[10] This method is applicable in the presence of silica, and has proved very efficient. We have not found the Volhard procedure to be satisfactory in this work.

Finally the several products obtained by the fluorination of the ethyl chloride were analyzed and results are summarized in Table II.

TABLE II

ANALYTICAL VALUES

Compd.	Calcd. F	Calcd. Cl	Found F	Found Cl
CF_2Cl_2[a]	31.4	58.7	31.4 ...	58.7 ...
CF_3Cl	54.5	34.0	54.6 54.3	34.0 34.0
CF_3CF_2Cl	61.5	23.0	61.4 61.5	23.1 23.1
$CF_2{=}CCl_2$	28.6	53.4	28.6 28.6	53.3 53.6
CHF_2CH_2Cl[b]	37.8	35.3	37.8 38.0	35.2 ...

[a] Analysis of purified Freon, to test the procedure. [b] Decomposed in a Parr bomb.

These results leave no doubt as to the composition of the compounds which were isolated in this work.

Summary

Ethyl chloride was fluorinated in the vapor phase over copper gauze under varying conditions, and the relative amounts of the more important products determined.

The compounds CF_4, CF_3Cl, CF_3CF_2Cl, $CF_2{=}CCl_2$ and CHF_2CH_2Cl were isolated from the reaction mixture. The last three of these have not been obtained before by the action of elementary fluorine on an organic compound.

A precise analytical procedure for determining fluorine and chlorine in stable organic gases has been described.

DURHAM, NORTH CAROLINA RECEIVED AUGUST 4, 1939

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[10] Kolthoff, Lauer and Sunde, THIS JOURNAL, 51, 3273 (1929).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Electrostatic Influence of Substituents on Reactions Rates. I

BY F. H. WESTHEIMER AND MARTIN W. SHOOKHOFF

Ingold has postulated that the effect of a polar substituent on the rate of saponification of an aliphatic ester, like the effect of such a substituent on the ionization constant of an acid, is largely electrostatic. In 1930[1] he employed Bjerrum's quantitative electrostatic formulation[2] to compute, from the ratios of the rates of saponification of the first and second ester groups, the separation of the carbalkoxy groups in a series of esters of dibasic acids. Ingold's evidence went far toward establishing his hypothesis in those cases in which the molecule is long and the substituent can be regarded as a negative charge.

Kirkwood and Westheimer[3] have recently refined Bjerrum's approximate computations of the electrostatic free energy involved in a chemical reaction; the success of the new equations, while general, has been most conspicuous in the considerations of the ionization constants of short dibasic and of dipole substituted acids,[4] cases for which the older formulation is inadequate. The shortcomings of Ingold's modified equation[5] have been presented previously.

The present paper deals with the rate of alkaline hydrolysis of esters and amides in cases in which the substituent is a negative charge, a positive charge and a dipole, all placed close to the seat of the reaction. When the substituent is close to the ester or amide bond that is broken, the rates of hydrolysis of the substituted and unsubstituted compounds differ by a factor of a hundred or more. Since the measurements were made by conductivity, very slow and very fast reactions were excluded: the former because of action of alkali on the glass of the cell, the latter because of the time required to attain thermal equilibrium. These considerations necessitated a careful selection of the pairs of compounds employed.

To illustrate the effect of a negative charge as substituent, the rate of alkaline hydrolysis of the sodium salt of oxamic acid was compared with the rate for oxamide; to illustrate the effect of a positive charge, the rate of saponification of the chloride of the tertiary butyl ester of betaine was compared with the rate for the tertiary butyl ester of dimethylglycine; and to illustrate the

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[1] Ingold, *J. Chem. Soc.*, 1375 (1930), 2170 (1931); Ingold and Mohrhenn, *ibid.*, 1482 (1935).

[2] Bjerrum, *Z. physik. Chem.*, **106**, 219 (1923).

[3] Kirkwood and Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); Westheimer and Kirkwood, *ibid.*, **6**, 513 (1938).

[4] Westheimer and Shookhoff, THIS JOURNAL, **61**, 555 (1939); Westheimer, *ibid.*, **61**, 1977 (1939); *cf.* Eucken, *Z. angew. Chem.*, **45**, 203 (1932).

[5] Ingold, *J. Chem. Soc.*, 2179 (1931).

effect of a dipole, the rate of saponification of the tertiary butyl ester of chloroacetic acid was compared with the rate for the tertiary butyl ester of acetic acid.

The equations of Kirkwood and Westheimer apply accurately only to spheres and to prolate ellipsoids in which substituents and charges are at the foci. Due to the experimental limitations mentioned above, some sacrifice in the shape of the molecule was unavoidable.

Theoretical

Ingold treated the reaction velocity problem by means of Christiansen's theory,[6] that is, as a case in which the local concentration of hydroxide ions differs, due to the presence in the molecule of a polar substituent, from that in the remainder of the solution. The assumptions involved can be more conveniently stated, however, when the problem is formulated in Brönsted's terms.[7]

Brönsted postulated a rapid equilibrium between the reactants and an activated complex, followed by a slow decomposition of the activated complex to form the reaction products. In order to apply the electrostatic theory, it is further necessary to assume that the rates of decomposition will be the same for activated complexes formed from two closely similar molecules.[8] Stated mathematically

$$k_{\text{obsd.}} = kK \text{ and } k'_{\text{obsd.}} = k'K'$$

$k_{\text{obsd.}}$ and $k'_{\text{obsd.}}$ are the observed velocity constants, corrected to infinite dilution, for the bimolecular reactions, and K and K' are the equilibrium constants for the formation of the two activated complexes. If k and k', the rate constants for the decomposition of the activated complexes, are assumed equal, then

$$k_{\text{obsd.}}/k'_{\text{obsd.}} = K/K'$$

In other words, to compute the ratio of the velocity constants at infinite dilution, it is only necessary to compute the ratio of the equilibrium constants for the formation of the critical complexes.

The rest of the argument exactly parallels that given by Kirkwood and Westheimer[3] for the case of the ionization constants of acids with and without polar substituents. $\boldsymbol{k}''T \log_e K - \boldsymbol{k}''T \log_e K'$ is equal to $\Delta w'$, where $\boldsymbol{k}''$ is Boltzmann's constant, T the absolute temperature, and $\Delta w'$ is the average reversible work expended in the transfer of a hydroxide ion from the unsubstituted activated complex to the substituted ester, infinitely separated in the solvent. Part of $\Delta w'$ is an entropy term, arising from differences in molecular symmetry. The electrostatic part of $\Delta w'$, called Δw, is that which can be computed. The part of $\Delta w'$ connected with the intrinsic structure of the molecules is by no means to be overlooked, but it is assumed that, as a first approximation, it will vanish because of cancellations between the substituted and unsubstituted compounds.

It follows, therefore, that

$$\Delta w = \boldsymbol{k}''T \log_e K/\sigma K' = \boldsymbol{k}''T \log_e k/\sigma k' = 2.303\ k''T\ \Delta \log k$$

where $\boldsymbol{k}''$ is the Boltzmann constant, σ is a statistical factor (equal to two in the saponification of esters or amides of dibasic acids) and the equation serves to define $\Delta \log k$.

From the equations of Kirkwood and Westheimer and from the experimental values of $\Delta \log k$, it is possible to compute the distance between the negative charge in the activated complexes, and the positive charge in the chloride of tertiary butyl betaine, the center of the dipole in tertiary butyl chloroacetate, and a positive charge in oxamide, located approximately in the position of the ionizable proton in oxamic acid. These distances are then compared with those obtained from an independent source.

Experimental

Apparatus.—Conductivity was measured with a calibrated Leeds and Northrup bridge, using a slide wire of the Kohlrausch type, and a Clough–Brengle audio frequency oscillator as the source of current. The apparatus was slightly modified[9] from the standard Washburn type, and was capable of measuring resistances with a precision of 0.01%.

The design of the conductivity cells was dictated primarily by the experimental observation that the percentage time rate of change of conductivity due to the solution of the glass in alkali increases with temperature, dilution, and the ratio of surface to volume, as shown in Table I. Cell A, used at alkali concentrations of 0.0003 to 0.003 was spherical, of one liter capacity, and had bright electrodes, 1.8 cm. in diameter and 2 cm. apart. Due to the large size of this cell, at least an hour was necessary to attain temperature equilibrium; it was not, then, very satisfactory for the more rapid reactions. For the concentration range 0.003 to 0.05, cell B was used. It was cylindrical in shape, 3 cm. in diameter and 11 cm.

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[6] Christiansen, *Z. physik. Chem.*, **113**, 35 (1924).

[7] Brönsted, *Chem. Rev.*, **5**, 231 (1928).

[8] The application of electrostatic theory to the problem of the change of rate with solvent involves a more limited assumption (Scatchard, *J. Chem. Phys.*, **7**, 657 (1939)). Since the transmission coefficient is usually in the neighborhood of unity, a broader assumption is involved in Eyring's theory (*ibid.*, **3**, 107 (1935)).

[9] Jones and Josephs, THIS JOURNAL, **50**, 1049 (1928).

long, with lightly platinized electrodes 1 cm. in diameter and 8 cm. apart. Cell C was 8 cm. longer than cell B, and the electrodes were 8 cm. further apart; the cells were otherwise identical. Cell D was designed according to Jones and Bollinger.[10] The electrodes were unplatinized and their area and the distance between them were approximately the same as for cell A.

An oil thermostat controlled the temperature to 0.01°.

TABLE I

RATE OF CHANGE OF CONDUCTIVITY OF SODIUM HYDROXIDE SOLUTIONS DUE TO SOLUTION OF GLASS

Cell	Alkali concn., N	Change in % per hr., at 30°	35°
A	0.002	0.022	
B	.005	.064	
B	.008		0.10
B	.030	.022	
C	.015	.030	.050
C	.050	.012	

Materials.—Tertiary butyl acetate was prepared according to Skrabal and Hugetz,[11] oxamide according to Liebig[12] and oxamic acid according to Oelkers.[13] Dimethylglycine was synthesized by the method of Michaelis and Schubert[14] and the chloride of betaine amide by the method of Renshaw and Hotchkiss.[15] To determine its purity, each was analyzed before use.

Tertiary Butyl Chloroacetate.—While the tertiary butyl chloroacetate used in the velocity determinations was prepared by direct esterification, a more convenient method of preparation follows: 60 cc. of chloroacetyl chloride was placed in a three-necked flask equipped with thermometer, stirrer, dropping funnel and an outlet protected by a calcium chloride tube. A mixture of 100 cc. of dimethylaniline and 75 cc. of tertiary butyl alcohol (m. p. 23°) was added dropwise during the course of an hour, maintaining the temperature at 0° by means of an ice-bath. At the end of this time, the ice-bath was removed and the mixture allowed to stand overnight. Water was then added, and the heavy ester layer separated, washed with water, dilute hydrochloric acid, sodium bicarbonate solution, and water again. The oil was dried over calcium chloride and vacuum distilled: yield, 72 g., or 60%, of the ester. The product is a colorless liquid, slightly heavier than water, boiling at atmospheric pressure at 155° with some decomposition and at 60.2° at 15 mm., n^{20}D 1.4230.

Anal. Calcd. for $C_6H_{11}O_2Cl$: C, 47.8; H, 7.37; Cl, 23.56; sapon. equiv., 150.5. Found: C, 47.6; H, 7.33; Cl, 23.63; sapon. equiv., 150.6.

The material actually used in the velocity determinations had been carefully fractionated at reduced pressure, and was of analytical purity.

An acidified portion of completely saponified ester gave no precipitate with silver nitrate, showing that there is no appreciable hydrolysis of the chlorine during saponification. Another portion of the ester was hydrolyzed, the tertiary butyl alcohol isolated, dried, and identified by melting point and the melting point of a mixture with an authentic sample.

Tertiary Butyl Betainium Chloride.—Twenty grams of tertiary butyl chloroacetate and 62 cc. of a 2.5 molar solution of trimethylamine in dry benzene were mixed with cooling. Although crystals formed in a few minutes, it proved advisable to allow the mixture to stand for twenty-four hours; yield, 18 g. The crude material can be crystallized from acetone or dioxane to which a small amount of water has been added. The product is a white crystalline powder, which, when dry, melts with decomposition around 220°, the exact temperature depending somewhat on the rate of heating.

Anal. Calcd. for $C_9H_{20}O_2NCl$: Cl, 16.91; N, 6.68. Found: Cl, 16.89; N, 6.79.

The material used in the rate determinations had been recrystallized several times, and was of analytical purity.

Tertiary Butyl Dimethylglycinate.—Twenty grams of tertiary butyl chloroacetate and 43 cc. of a 4 molar solution of dimethylamine in dry benzene were mixed, with cooling, and allowed to stand at room temperature for twenty-four hours. The resultant material was extracted with 1:1 hydrochloric acid, and the extract washed once with ether. The aqueous layer was then saturated with potassium carbonate and extracted with ether. The ether extract was dried with potassium carbonate, the ether removed by distillation, and the residue fractionated at reduced pressure. The yield of colorless oil, having a slight ammoniacal odor, was 12 g. The hydrochloride was prepared by adding a slight excess of hydrogen chloride in methanol, and evaporating to dryness under reduced pressure. The residue can be recrystallized from a 10% solution of tertiary butyl alcohol in benzene. The white twice recrystallized material which was used in the velocity determinations melted about 150°, the exact temperature depending somewhat on the rate of heating.

Anal. Calcd. for $C_8H_{18}O_2NCl$: Cl, 18.13; N, 7.16. Found: Cl, 18.08; N, 7.12.

Conductivity water and carbonate free alkali were used throughout. Chemicals other than those recorded here were of reagent grade.

Method.—The usual procedure in the determination of reaction velocity by conductivity is to determine the initial and final conductivities of the solution and to calculate the rate on the assumption that the conductivity of the solution is a linear function of the extent of reaction. In the determinations here described, since it was inconvenient in most cases to measure the initial and final conductivity, each velocity determination was standardized by measuring the conductivity of solutions corresponding in ionic composition to that present at several different times during the reaction.[16] Since the concentrations of the various ions in the standardizing-solution could not conveniently be made exact

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(10) Jones and Bollinger, THIS JOURNAL, **53**, 411 (1931).

(11) Skrabal and Hugetz, *Monatsh.*, **47**, 17 (1926).

(12) Liebig, *Ann.*, **9**, 1 (1834); see "Beilstein," IV ed., Vol. II, p. 546.

(13) Oelkers, *Ber.*, **22**, 1566 (1889).

(14) Michaelis and Schubert, *J. Biol. Chem.*, **115**, 221 (1938).

(15) Renshaw and Hotchkiss, THIS JOURNAL, **48**, 2698 (1926).

(16) A similar standardization procedure has been described by Crocker and Lowe, *J. Chem. Soc.*, **91**, 952 (1907).

duplicates of those at any point during the reaction, a small correction had to be added to the conductivity of each standardizing solution. In order to estimate this correction, it was only necessary to know the ratios of the conductivities of all the ions present to that of hydroxide ion.

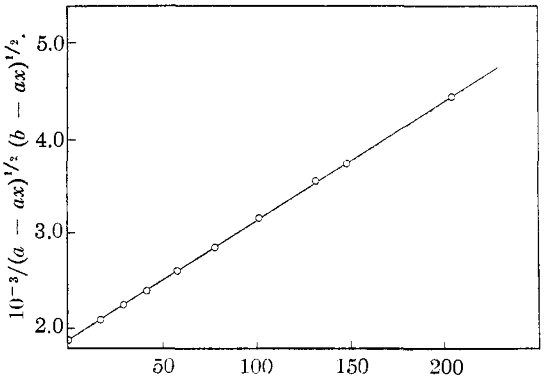

Fig. 1.

The values of the conductances are given in Table II, arbitrarily assigning to hydroxide ion a value of 100 at every temperature. The values in the upper part of the table were calculated from existing data,[17] those in the lower part of the table were measured. Since the correction was in all cases small, comparatively large errors in the relative conductivities of the ions do not affect the final result appreciably. The measurements were made in an ionic environment similar to that in the actual reaction mixtures, except in the case of tertiary butyl betainium chloride, which was measured in a solution containing only the pure compound.

TABLE II

RELATIVE CONDUCTIVITIES OF THE IONS

Ion	Temperature		
	6.5°	10°	30°
Hydroxide	100.0	100.0	100.0
Chloride	39.0	38.7	
Acetate	20.6		
Oxalate			70.3
Sodium	24.7	24.7	24.7
Ammonium			35.6
Chloroacetate	16.6		
Oxamate			18.7
Dimethylglycinate	12.5		
Betaine amide	19.8		
t-Butylbetainium	17.8		

In some cases there was a slow reaction between the ions of the standardizing solutions. Since the extent of the reaction was always quite small, it was not difficult to extrapolate accurately back to the time when the solution was prepared. The procedure could not be used for tertiary butyl betainium chloride, because of the rapid reaction of the positive ion with alkali; therefore the corresponding amide was used in place of the ester. After determining the relative conductivities of the ester and amide ions, it was possible to estimate the conductivities of the solutions used in the reaction velocity determinations. While the error in this case is probably greater than in any other, it cannot be large, since only 10% of the total conductivity is contributed by the positive ion.

Results

The data for a typical velocity determination, the saponification of tertiary butyl chloroacetate, are given in Table III. Here a is the initial concentration of sodium hydroxide in moles per liter, b the initial concentration of the ester, and x the fraction of the alkali consumed in time, t. The rate constants were obtained graphically by plotting time against $\log(1 - x)/(b - ax)$, or, when the initial concentrations of the two reactants were nearly equal, against $1/(a - ax)^{1/2}(b - ax)^{1/2}$. Figure 1 is a graph of the data in Table III.

TABLE III

DATA FOR THE SAPONIFICATION OF TERTIARY BUTYL CHLOROACETATE

$a = 0.000782$ Time in min.	$b = 0.000835$ Conductivity	x
0.0	4462	0.346
17.4	4165	.420
29.1	4000	.461
41.4	3851	.498
57.3	3683	.540
77.3	3510	.583
101.2	3334	.627
131.6	3170	.667
147.7	3094	.686
203.8	2887	.738
262.9	2727	.778

Conductivity in this case is a linear function of the extent of reaction. When $x = 0.010$ the conductivity is 5813 and when $x = 0.660$ the conductivity is 3197. The conductivities are all in arbitrary units.

The solution of glass in alkali changes both the conductivity and the hydroxide-ion concentration. In correcting for the former effect, it was assumed that the percentage time rate of change of conductivity due to reaction with the

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(17) Landolt–Börnstein, "Physikalisch-chemische Tabellen," Erg. IIIc.

TABLE IV

SUMMARY OF THE VELOCITY DETERMINATIONS

Organic reactant	Cell	a	b	μ	T	k in min.$^{-1}$ (mols/l.)$^{-1}$
Oxamide	B	0.004669	0.003207	0.00467	30.1°	1.36
	A	.002076	.001301	.00208		1.40
						Av. 1.38
Sodium oxamate	C	.05504	.05492	.110	30.1°	0.0158
	B	.03209	.02676	.0589		.0143
	B	.02732	.01738	.0447		.0138
	C	.01424	.01197	.0262		.0132
				Value for infinite dilution		.0101
t-Butyl dimethylglycinate	B	.01408	.01618	.0303	10.2°	.0220
	B	.00731	.00866	.0160		.0228
						Av. .0224
t-Butyl betainium chloride	D	.002143	.002112	.00426	10.2°	23.5
	D	.000849	.00776	.00163		23.8
	D	.000841	.00835	.00168		21.0
	A	.000596	.000593	.00119		(18.9)
	D	.0005042	.0004880	.000992		20.7
	A	.0005042	.0004880	.000992		20.8
	D	.0004354	.0004288	.000864		23.2
						Av. 22.2
t-Butyl acetate	B	.03181	.01981	.0318	6.6°	0.0247
	B	.01421	.04087	.0142		.0254
	A	.002269	.01421	.00227		.0244
						Av. .0248
t-Butyl chloroacetate	D	.000782	.000835	.000782	6.6°	11.9
	A	.000629	.000587	.000629		(14.4)
	D	.000582	.000570	.000582		21.1
	A	.000582	.000570	.000582		12.5
	D	.0004362	.0004405	.000436		12.4
						Av. 12.2

glass is constant during a given experiment. In correcting the latter, the hydroxide-ion concentration at each point was reduced by a factor of $1 - pt$, where p is the percentage time rate of change of hydroxide ion and t the time. It was assumed that the change in hydroxide-ion concentration was 1.6 times the change in conductivity given in Table I. While neither of these computations is exact, the total correction is so small that the methods used will cause no serious errors.

In the case of the saponification of the ester of dimethylglycine, the base formed, dimethylglycinate ion, contributes to the hydroxide-ion concentration. So does the ammonia formed in the hydrolysis of sodium oxamate and of oxamide. Furthermore, in this latter case, the hydrolysis of the second amide group will be a complicating factor. However, these corrections are so small that the values of the velocity constants obtained using a standard bimolecular form are not significantly different from those obtained by more complicated equations in which these corrections are, at least to a first approximation, embodied.[18]

The constants for all the velocity determinations are collected in Table IV. Here μ is the initial ionic strength, k the rate constants in inverse minutes and inverse moles per liter. The initial concentrations were varied at least twofold; the constants usually deviate less than 5% from the average. The values in parentheses were not used in averaging.

The observed rate constants for the hydrolysis of sodium oxamate increase with increasing ionic

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(18) For the hydrolysis of sodium oxamate and the tertiary butyl ester of dimethylglycine, for example, the following equation takes into account the ionization of the base.

$$kt + C = \frac{1}{[a(a-b)^2 + a^2K_B]}\left\{ - a(a - b + K_B)\log_e(b - ax) + \frac{a(a - b + K_B)}{2}\log_e[a(1-x)^2 + K_B] + b\sqrt{aK_B}\tan^{-1}\frac{ax - a}{\sqrt{aK_B}}\right\}$$

Here a is the initial concentration of sodium hydroxide, b that of the ester, k is the rate constant, K_B the ionization constant of the base, and x the fraction of the sodium hydroxide that has been consumed at time, t. C is a constant of integration. When the second stage hydrolysis of oxamide is taken into account, the equation is even more complex.

strength. Since the reaction is one between two negative ions, Brönsted's theory[7] predicts a positive primary salt effect. However, at the ionic strengths at which the measurements were made, the observed salt effect is less than the theory predicts. Extrapolation of the plot of log $k_{\text{obsd.}}$ against the square root of the ionic strength gives a value of 0.0111 for the rate constant; extrapolation of the lowest point using the theoretical limiting slope gives a value of 0.0091. These are an upper and lower value, respectively, for the true value at infinite dilution. For the purposes of the present paper, the mean value, 0.0101, is sufficiently precise. Since the saponification of tertiary butyl betainium chloride was carried out at very low ionic strength, and since the accuracy of these measurements is not very great, extrapolation to infinite dilution does not seem warranted.

The ion $(CH_3)_2N^+HCH_2CO_2C(CH_3)_3$ would be expected to saponify at a rate several hundred times greater than that of the free base. However, an estimate of the base strength of the ester (from the base strength of glycine ethyl ester[19]) indicates that, in solutions of the alkalinity employed in the velocity determinations, no significant part of the rate can be due to hydrolysis of this ion.

The logarithms of the ratios of the rates, corrected for statistical factor, for substituted and unsubstituted compounds (Δ log k) are assembled in Table V. It is at once obvious that errors of the magnitude indicated for the velocity constants will have no significant effect upon these logarithms.

Discussion of Results

From the data given in Table V and Kirkwood's and Westheimer's equations, it is possible to compute the separation of the polar substituent and the negative charge contributed by the hydroxide ion to the activated complex. In order to carry out these calculations, the volumes of the molecules have been estimated, as usual, by using Traube's rule.[20]

Table V

Separation of Charge and Substituent, Computed from Velocity Data

Organic reactants	Δ log k	Separation in Å.		
		R	R_D	R_B
Oxamide Sodium oxamate	1.84	4.15	3.85	1.71
t-Butyl betainium chloride *t*-Butyl ester of dimethylglycine	3.02	4.85	4.05 (glycine) 4.25 (betaine)	1.02
t-Butyl chloroacetate *t*-Butyl acetate	2.70	3.15	3.00	0.48

The computations for oxamide were made on the basis of a spherical model, with the charges on a diameter. The distance between a positive charge placed approximately as the proton in oxamic acid, and the negative charge of the activated complex, is given to the nearest 0.05 Å. by R; it is compared with R_D, the separation of the protons in oxalic acid computed in a similar manner from dissociation constant measurements.

The calculations for tertiary butyl chloroacetate are more complicated. The difference between the carbon–chlorine dipole moment and the carbon–hydrogen moment was taken as 1.86 Debye units.[21] The negative charge of the activated complex was placed arbitrarily on the extension of that carbon to carbon bond nearest the ester linkage in the acid portion of the molecule. The computations were made on the basis of two different assumptions. First, the charge and dipole were placed equidistant from the center on a diameter, and, second, the charge was placed at the center of the molecule.[22] The two methods led to values of R differing by 0.4 Å.; the average is given in Table V. The value of R_D is that obtained from computations based on the ratio of the ionizations constants of chloroacetic and acetic acids.

The computations for the chloride of the tertiary butyl ester of betaine were made both on the basis of an ellipsoid with the charges at the foci, and on the basis of a sphere, with the charges on a diameter, but the positive charge twice as far from the center of the sphere as the negative charge.[23] Again the two methods give values

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(19) Edsall and Blanchard, This Journal, **55**, 2337 (1933).

(20) Traube, *Saml. Chem. Chem.-tech. Vortr.*, **4**, 255 (1899).

(21) Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

(22) In this case, the equation for the electrostatic work reduces to the form

$$\Delta \log k = \frac{eM \cos \zeta}{2.303\, \boldsymbol{k}'' T R^2 D_i}$$

where e is the electronic charge, M the dipole moment of the substituent, ζ the angle between the dipole and the line joining it to the center. D_i the "internal dielectric constant," has been assigned the value of 2.00, as previously.

(23) In this case the appropriate value of the "effective dielectric constant" is given by the equation

$$1/D_E = \frac{1}{D_i}\left[1 - \frac{x_1 + x_2}{1 + x_1x_2}\right] + \frac{1}{D}\left[\frac{2(x_1 + x_2)}{1 + x_1x_2} - \frac{x_1 + x_2}{x_1x_2}\log_e(1 + x_1x_2)\right]$$

where $x_1 = r_1/b$ and $x_2 = r_2/b$. r_1 and r_2 are the distances of the first and second charges from the center, b the radius of the sphere.

differing by about 0.3 Å.; the average appears in the table.

There is no value of R_D obtained from ionization constant data which is strictly comparable with this value of R. For, while the ionization constant of betainium chloride is known, the ionization constant of dimethylglycine, due to its zwitterionic structure, cannot be considered that of the corresponding unsubstituted acid. However, the strength of betainium chloride was compared with that of trimethylacetic acid,[17] the "isosteric" structure,[24] in which a carbon atom rather than a nitrogen atom holds the three methyl groups. Neuberger's data show that this is a fair approximation.[25] The length given in Table V is the average of one in which the molecule is regarded as an ellipsoid with charges at the foci, and one in which the molecule is regarded as a sphere with the charges equidistant from the center on radii separated by the tetrahedral angle. Fortunately, these two values of R_D differ by only 0.3 Å. The value of R_D for glycine is placed alongside the approximate one for betaine.

The values of R_B were computed using Bjerrum's[2] and Eucken's[4] equations. In the case of the chloroester, the fully extended model was used in determining the value of R_B.

Inspection of Table V reveals that, despite the approximations made in assigning simple shapes to these esters and amides, the values of R obtained from velocity data are in good agreement with R_D, computed from dissociation constants. It must be stressed that these latter values have previously been shown in all cases to be of reasonable magnitude. The values of R_B, obtained from the Bjerrum equation, are, however, much too small. Since R appears as the square in the equation for the potential of a dipole, the inadequacy of the simple equation in the case of the chloroester, serious as it appears, is actually even more significant.

The retardation caused by a negative charge, the acceleration caused by a positive charge and a dipole in saponification, are not only qualitatively but quantitatively in accord with predictions made on the basis of the electrostatic effect of the substituents.

Summary

1. The electrostatic theory has been applied to the problem of the effect of polar substituents on reaction velocities.

2. The rates of alkaline hydrolysis of the following pairs of compounds have been measured: oxamide and sodium oxamate, tertiary butyl acetate and tertiary butyl chloroacetate, the tertiary butyl ester of dimethylglycine and the chloride of the tertiary butyl ester of betaine.

3. By means of the equations previously developed by Kirkwood and Westheimer, it has been shown that the ratio of the rates for each pair is quantitatively in accord with the hypothesis that the effect of a polar substituent on the velocity of these hydrolyses is primarily electrostatic in origin.

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[24] Schwarzenbach, *Z. physik. Chem.*, **A176**, 133 (1936).

[25] Neuberger, *Proc. Roy. Soc.* (London), **A158**, 68 (1937).