dissolved substance in moles/liter at time t—the first order diffusion equation has the same form as a zero order rate equation.

The fact that making the sodium anodic slows up the dissolution process and causing the sodium to be cathodic accelerates this reaction shows that the dissolution process is of an electrochemical nature. With the dissolution of most metals in an aqueous solution, if the metal is made cathodic, then the anodic reaction—that of the oxidation of the metal to form ions—is inhibited. Evidently, in the case of sodium dissolving in liquid ammonia the slowest step of the dissolution process is the cathodic reaction, which, according to the so-called solvated electron theory[9,10,11] would be the association of varying amounts of ammonia with the liberated electrons. However, the solvated electron theory in conjunction with the experimental facts of anodic and cathodic charges help only in the speculations as to the nature of the process and offer no definite proof as to the mechanism of the dissolution process.

Acknowledgment.—This work was done as part of a contract with the U. S. Army Signal Corps, Squier Signal Laboratory, Fort Monmouth, New Jersey, under contract No. W-36-039-sc-32065.

Conclusions

The conclusions which can be drawn from this investigation are: 1. The data appear to fit a zero order and a first order equation about equally well.

2. The apparent energy of activation of 4.2 kcal. is relatively low, showing that a diffusion process is possible.

3. An increase in the linear velocity of the metal specimen increases the reaction rate. At 40° the functional relationship is $k = (1.13 \times 10^{-7}) v + 7 \times 10^{-5}$ thus showing that a diffusion process is probable.

4. Charging the sodium alters the dissolution rate.

5. These points support the view that within the range of concentration, linear velocity, pressure and temperature which were encountered in the experimental work, the dissolution process is of an electrochemical nature which is under diffusion control and therefore first order.

Chicago, Illinois Received August 1, 1949

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[9] Charles A. Kraus, This Journal, **36**, 871 (1914).

[10] Charles A. Kraus and Walter W. Lucasse, *ibid.*, **43**, 2529 (1921).

[11] W. Conard Fernelius and George W. Watt, *Chem. Rev.*, **20**, 195 (1937).

[Contribution from The Institute of Paper Chemistry]

The Rate of Esterification of Primary and Secondary Hydroxyls of Cellulose with *p*-Toluenesulfonyl (Tosyl) Chloride[1]

By Emil Heuser,[2] Merle Heath and Wm. H. Shockley

Formation of the *p*-toluenesulfonyl or tosyl ester offers a possible means for measuring the relative rates of esterification of the primary and secondary alcoholic groups of cellulose. Since it has been shown that the tosyl ester in the primary position in glucose is replaceable by iodine on treatment with an excess of sodium iodide in a suitable medium,[3] a number of investigators have applied this method to cellulose derivatives[4–7] and cellulose,[7–8] also, in order to determine the distribution of tosyl groups between the primary and secondary positions. Evidence has recently been published,[8] however, which indicates that the distinction between primary and secondary hydroxyl groups by this method is not exact under all conditions; analyses of some of the products imply the introduction of slightly more than one iodine atom per glucose unit into tosylated cellulose.

In the present work, a chemically reactive cellulose was prepared by regeneration of cotton linters from a solution of cellulose xanthate, replacing the water successively with methanol, ethyl ether and, finally, cyclohexane. This sequence of solvent replacements has previously been used by Staudinger and Mohr.[9] Samples swollen in pyridine were esterified with a solution of tosyl chloride (amounting to 10 moles per anhydroglucose unit) in pyridine for various periods of time at 25°. The tosyl derivatives were then treated with sodium iodide in acetonylacetone at 115–120°,[5–6] after which they were analyzed for combined iodine and combined tosyl (sulfur).

Because the degree of substitution of the sample with the longest esterification time (ten hours) was still less than one group per anhydroglucose unit, another sample of reactive cellulose was prepared by the same method and a second series of tosylations and iodine replacements was made, this time including esterification periods up to fifty hours. Data from the two series were fairly consistent and indicated that the rate of reaction of both primary and secondary hydroxyls was proportional to the concentration of free hydroxyls of

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[1] A portion of this work was carried out in connection with U. S. Army Quartermaster Corps Contract No. W44-109-qm-1209 (O. I. No. 2963).

[2] Present address: 339 Vista de la Playa, La Jolla, California.

[3] Oldham and Rutherford, This Journal, **54**, 366 (1932).

[4] Cramer and Purves, *ibid.*, **61**, 3458 (1939).

[5] Mahoney and Purves, *ibid.*, **64**, 9, 15 (1942).

[6] Gardner and Purves, *ibid.*, **64**, 1539 (1942).

[7] Honeyman, *J. Chem. Soc.*, 168 (1947).

[8] Malm, Tanghe and Laird, This Journal, **70**, 2740 (1948).

[9] Staudinger and Mohr, *Ber.*, **70**, 2299 (1937).

these respective types—that is, the equations for first order reactions were followed (in the presence of an excess of tosyl chloride) with the rate of esterification of the primary hydroxyls being 5.8 times that of secondary hydroxyls.

Designating the substitution of primary hydroxyl groups per anhydroglucose unit by S_P and that of secondary hydroxyl groups by S_S, with t representing the time of esterification in hours

$$\log [1/(1 - S_P)] = 0.0260t$$
$$\log [2/(2 - S_S)] = 0.045t$$

Previous investigators,[4-6] studying the *homogeneous* tosylation of partially substituted cellulose derivatives dissolved in pyridine, have found a greater difference than this between the rate of tosylation of primary and secondary hydroxyl groups. Mahoney and Purves[5] calculated for ethylcellulose containing 0.52 free hydroxyl group per glucose unit first order reaction constants of 0.07, 2.3 and 15 for the substitution on positions 3 and 2 (secondary), and 6 (primary), respectively. Gardner and Purves[6] calculated for cellulose acetate containing 0.56 free hydroxyl group per glucose unit first order reaction constants of 0.106, 2.16 and 23.4 for substitution on the same positions.

In the present work, which deals with a *heterogeneous* tosylation of cellulose itself, the reaction rates obtained may not represent the actual differences in chemical reactivity of the primary and secondary hydroxyls but may be affected by differences in accessibility of the various hydroxyls in the cellulose structure.

Experimental

Cellulose.—Bleached commercial cotton linters from the Hercules Powder Co.—α-cellulose 98.3%, ash 0.06%, copper number 0.13, degree of polymerization (D. P.) by the nitrate method approximately 1500. The D. P. was determined by a modification of the technique used by Atchison[10]; that is, the cellulose was converted to the nitrate, and the solution viscosity of a very dilute solution in acetone was determined with a constant overflow type modified Ostwald viscometer. The molecular weight and the D. P. of anhydroglucose units were then calculated from the specific viscosity, using the Staudinger function and a K_m value of 11×10^{-4}.

This starting material was converted into a cellulose xanthate solution by the method of Jayme and Wellm,[11] except that ten times the quantities (32 g. of cellulose) were used. For the first series the cellulose xanthate solution was diluted to twice its weight with water and then filtered through a muslin cloth to remove any undissolved fibers. The filtered solution was precipitated into water containing 8% sulfuric acid and 24% sodium sulfate by means of a high-speed agitator or Waring Blendor. The regenerated cellulose precipitate was washed, desulfurized in a solution containing 0.8% sodium sulfide and 0.4% sodium hydroxide, and thoroughly washed again. The water was replaced by methanol, the methanol by ethyl ether, and the ethyl ether by cyclohexane. Each replacement was made three times. Finally, after removing as much of the cyclohexane as possible by suction, the regenerated cellulose was dried overnight in a vacuum oven at 50°, and subsequently kept in a desiccator. The average D. P. of this material, as determined by the nitrate method, was approximately 435. For the second series, the cellulose xanthate solution was prepared in the same way but, instead of filtering, it was centrifuged at 2000 r. p. m. and the clear solution decanted from the undissolved portion. The average D. P. of the second sample of regenerated cellulose was approximately 785. It would thus seem that more oxidation, and hence degradation, occurred during the preparation of the first sample, probably during the filtering operation. No sulfur was found in either sample.

***p*-Toluenesulfonyl Chloride.**—Eastman Kodak Company (m. p. 66–68°), recrystallized from ethyl ether; for the second series, a technical grade, which was recrystallized several times from benzene and finally from ether, was used. The recrystallized material melted completely at 67–69°.

Pyridine Merck medicinal grade, dried over barium oxide and redistilled just before use.

Sodium Iodide Merck reagent grade, dried in the vacuum oven just before use.

Acetonylacetone.—Eastman Kodak Company product (b. p. 190–193°) was used as received for the first series. For the second series, the acetonylacetone (Cudner and O'Connor Co., Chicago) was redistilled *in vacuo*.

Tosylation Series A.—Ten samples (approximately 2 g. each) of the regenerated cellulose (D. P. 435) were weighed and placed in 250-ml. ground-glass stoppered flasks, 20 ml. of pyridine were added to each flask, and the mixtures allowed to stand overnight. *p*-Toluenesulfonyl chloride (235.35 g.) was dissolved in pyridine, brought to 25°, and made up to 500 ml. with pyridine. The flasks containing the cellulose and pyridine mixtures were suspended in a water-bath at 25°. To each flask was added 50 ml. of the pyridine-tosyl chloride solution (containing 23.5 g. of tosyl chloride or 10 moles for each anhydroglucose unit of cellulose), and the pipet was washed with 5 ml. of pyridine. The flask was shaken to mix the contents thoroughly and then replaced in a 25° water-bath.

Composition of the reaction mixture:

Cellulose	2.0 g. (0.1646 mole per liter)
Tosyl chloride	23.5 g. (1.646 moles per liter)
Pyridine	75 ml.

At the designated time, the flask was removed from the bath and cooled in an ice-bath for two minutes, after which 75 ml. of ice-cold acetone containing 7.5 ml. of water was added to decompose the remaining tosyl chloride. The mixture was shaken in ice water for five minutes and poured into 600 ml. of distilled water. The suspension was stirred for thirty minutes, after which it was filtered through a coarse fritted-glass filter and washed well with distilled water. The product was then suspended in about 600 ml. of distilled water and allowed to stand overnight. The next morning the sample was collected on a coarse fritted-glass crucible, washed, extracted with methanol and then with ethyl ether in a Soxhlet apparatus, after which the sample was air dried at room temperature and, finally, in a vacuum desiccator over phosphoric anhydride.

Series B.—The procedure was similar to that for the first series, except that the higher D. P. cellulose (785) was used and the weight of cellulose sample was increased to approximately 2.5 g. in order to have more product for analysis. Forty ml. of pyridine was placed on each sample, and the mixture was allowed to stand overnight. After adjusting the temperature to 25°, 29.4 g. of tosyl chloride in 55 ml. of pyridine was added.

Composition of the reaction mixture:

Cellulose	2.5 g. (0.1623 mole per liter)
Tosyl chloride	29.4 g. (1.623 moles per liter)
Pyridine	95 ml.

The samples after tosylation were very highly swollen and, after thirty hours, appeared to be on the verge of complete dispersion. In stopping the tosylation, it was found that cooling in the ice-water mixture for two minutes reduced the temperature of the reaction mixture to a little

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[10] Atchison, *Paper Trade J.*, **116**, no. 22, 23 (1943).

[11] Jayme and Wellm, *Kolloid-Z.*, **107**, 163 (1944).

under 20°. By adding 100 ml. of acetone containing 10 ml. of water slowly with continuous stirring, the maximum temperature during the operation was 35–40°. The final mixture was then precipitated into water in the high-speed agitator and was separated, washed, and extracted as before.

Iodination. Series A.—Approximately 1 g. (weighed on the analytical balance) of dry sodium iodide was dissolved in 100 ml. of acetonylacetone in a 250-ml. Erlenmeyer flask and heated to 115–120° in a glycerol-bath. The flask was fitted with an air condenser. After the solution had reached the bath temperature, approximately 1 g. of the tosylated cellulose sample was added. The temperature was maintained at 115–120° for seven hours. The flask was vigorously shaken about once every thirty minutes. At the end of seven hours, the mixture was filtered through a coarse fritted-glass funnel and the filtered sample was washed five times with 100-ml. portions of methanol. Then, 250 ml. of 0.1 *N* sodium thiosulfate was poured through; the material was removed from the filter, stirred twice with 250-ml. portions of 0.1 *N* sodium thiosulfate and, finally, washed on the filter again with a fourth portion to remove any adsorbed iodine. After thoroughly washing with distilled water, the product was extracted in a Soxhlet apparatus with ethyl ether as long as the ether showed any trace of color (from decomposition products of acetonylacetone). It was finally dried in a vacuum oven at 50° and then in a vacuum desiccator over phosphoric anhydride.

Series B.—In the second series, the procedure was modified to give a shorter reaction time and to avoid a possible loss of product through solution in the reaction mixture. The time was reduced from seven to four hours, since experiments indicated that iodine replacement was complete in that time. A 250-ml., 2-neck, round-bottom flask (with standard taper ground-glass joints) fitted with a glass thermometer well and an air condenser was heated with a Glas-Col heating mantle through a variable transformer. After the reaction period, the mixture was poured into 500 ml. of distilled water with continuous agitation. This step was included because it was found that the more highly tosylated samples were partially dissolved in the reaction mixture during the iodination. The product was then filtered, washed with water, 0.1 *N* sodium thiosulfate solution, and water, and then extracted with ethyl ether and dried as before.

Analytical Methods

Sulfur.[12]—Samples of 0.2 g. were fused with 15 g. of sodium peroxide, 1 g. of potassium perchlorate, 0.2 g. of sucrose and 0.2 g. of benzoic acid in the Parr bomb. The melt was taken up in hot water, acidified with concentrated hydrochloric acid and filtered. The sulfate was precipitated hot with 10% barium chloride solution. The precipitate was filtered and washed, dried and ignited to constant weight. There was no sulfur present in the blank determination.

Iodine.[13]—Samples of 0.1 g. in 20 ml. of potassium acetate in acetic acid were oxidized by heating with liquid bromine for thirty minutes, replenishing the bromine as necessary. (In the second series, it was found advisable to extend this time of heating with bromine until the material was apparently all in solution.) After cooling, the oxidized solution was diluted with 25 ml. of 25% sodium acetate solution and 100 ml. of water. The bromine was then reduced with several ml. of formic acid during a period of ten to fifteen minutes. Approximately 1 g. of potassium iodide and 10 ml. in 10% sulfuric acid were added, and the iodine liberated was titrated with 0.1 *N* sodium thiosulfate, using starch indicator. This method was checked in one experiment with the gravimetric method after fusion in the Parr bomb with sodium peroxide and potassium nitrate.[12] The blank showed no evidence of iodine.

Chlorine.—Parr bomb method.[12]

Results and Discussion

The data are presented in Tables I and II. The amount of chlorine introduced during the tosylation was not sufficient (maximum 0.3%) to interfere seriously with the calculations. The increased chemical reactivity of the regenerated cellulose is evident in a comparison with the original cotton linters in Series B for a tosylation period of one hour.

TABLE I

TOSYLATION OF CELLULOSE

Series A

Tosylated, hr.	Sulfur, %	Calcd. tosyl groups per glucose unit[a]
0.5	1.6	0.09
1.0	2.6	.15
1.5	2.65	.15
2.0	3.3	.20
3.0	4.2	.27
4.0	4.8	.32
5.0	5.7	.40
6.5	7.2	.56
8.0	8.1	.67
10.0	9.2	.83

Series B

Tosylated, hr.	*Sulfur,* %	Chlorine, %	Calcd. tosyl groups *per glucose* unit[a]
1.0[b]	1.0	0.0	0.05
1.0	3.8	.2	.23
5.0	5.7	.0	.40
10.0	7.7	.1	.62
20.0	10.8	.1	1.14
30.0	11.9	.1	1.41
40.0	12.1	.3	1.47
50.0	12.3	.3	1.52

[a] Calculated from $100/(162.14 + 154.18n_T) = \%S/32.05n_T$, where n_T equals tosyl groups per glucose unit. When one molecule of *p*-toluenesulfonyl chloride combines with one glucose unit of cellulose, the net gain in weight is 154.18, of which 32.05 is contributed by the sulfur atom. [b] Original cotton linters used in this one tosylation.

The total degree of substitution of the iodotosyl cellulose, calculated from the iodine and sulfur content, does not agree exactly with the original degree of substitution calculated from the sulfur content of the tosyl cellulose. It is usually a little lower. Blank experiments have indicated some loss in sulfur on heating tosyl cellulose to 115–120° with acetonylacetone, but whether the discrepancy represents an actual loss or is merely the result of analytical errors cannot be concluded at this time.

The excess of tosyl chloride used apparently eliminated its concentration in the system as a factor in the reaction rates, and a plot of the logarithm (to the base ten) of the free hydroxyl groups against time, shown in Fig. 1, gave a straight-line relationship for primary and secondary alcoholic groups, respectively, in conformity with the equation for a first order reaction. Unfortunately, the

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(12) Booklet 113, Parr Instrument Co., Moline, Illinois.

(13) E. P. Clark, "Semimicro Quantitative Organic Analysis," Academic Press, Inc., New York, N. Y., 1943, p. 62.

TABLE II

IODINATION OF TOSYL CELLULOSE

Tosylated, hr.	Iodine, %	Sulfur, %	Calcd. primary hydroxyls substituted per glucose unit[a]	Calcd. free primary hydroxyls per glucose unit	Calcd. sec. hydroxyls substituted per glucose unit[b]	Calcd. free secondary hydroxyls per glucose unit
			Series A			
0.5	4.7	0.5	0.06	0.94	0.03	1.97
1.0	7.3	.7	.10	.90	.04	1.96
1.5	8.4	.6	.12	.88	.03	1.97
2.0	10.4	.5	.15	.85	.03	1.97
3.0	13.7	1.6	.22	.78	.10	1.90
4.0	16.5	1.0	.26	.74	.06	1.94
5.0	18.8	1.3	.31	.69	.09	1.91
6.5	21.0	1.7	.36	.64	.12	1.88
8.0	24.7	1.8	.45	.55	.13	1.87
10.0	26.5	2.5	.52	.48	.20	1.80
			Series B			
1.0[c]	2.8	1.2	0.04	0.96	0.07	1.93
1.0	8.3	0.2	.12	.88	.01	1.99
5.0	17.6	1.2	.28	.72	.07	1.93
10.0	24.1	2.2	.45	.55	.16	1.84
20.0	30.0	3.5	.67	.33	.31	1.69
30.0	31.4	5.4	.86	.14	.58	1.42
40.0	31.9	5.8	.91	.09	.66	1.34
50.0	23.3	5.3	.55	.45	.49	1.51

[a] Calculated from $100/(162.14 + 154.18n_T + 109.92n_I) = \%\ \text{iodine}/126.92n_I$, where n_I equals moles iodine per glucose unit, with $n_T = 126.92n_I\ \%\ \text{sulfur}/32.05\%\ \text{iodine}$.
[b] Calculated from $100/(162.14 + 154.18n_T + 109.92n_I) = \%\ \text{sulfur}/32.05n_T$, where n_T equals moles tosyl per glucose unit, with $n_I = 32.05n_T\ \%\ \text{iodine}/126.92\%\ \text{sulfur}$.
[c] Original cotton linters used in this one tosylation.

analytical results for the longest tosylation period (fifty hours) are not consistent with the other samples and, therefore, have been omitted from the calculations. By means of the method of least squares, the slope of the line for primary hydroxyls was calculated to be 0.0260 and that for the secondary hydroxyls to be 0.0045, or a rate ratio of 5.8 in favor of the primary hydroxyls.

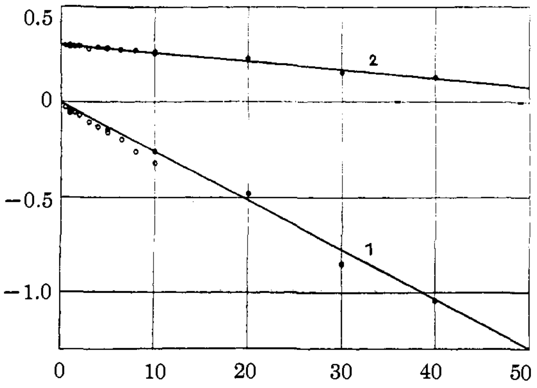

Fig. 1.—Rate of tosylation of cellulose: 1, primary hydroxyls; 2, secondary hydroxyls; ○, Series A; ●, Series B.

Representing the concentration of free primary hydroxyl groups per anhydroglucose unit by $c[\mathrm{OH}]_P$ and that of free secondary hydroxyl groups per anhydroglucose unit by $c[\mathrm{OH}]_S$, at any time t

$$t = \frac{1}{k_P} \log \frac{1}{c[\mathrm{OH}]_P}$$

and

$$t = \frac{1}{k_S} \log \frac{2}{c[\mathrm{OH}]_S}$$

Therefore

$$\frac{1}{k_P} \log \frac{1}{c[\mathrm{OH}]_P} = \frac{1}{k_S} \log \frac{2}{c[\mathrm{OH}]_S} \text{ and}$$

$$\log c[\mathrm{OH}]_S = \frac{k_S}{k_P} \log c[\mathrm{OH}]_P + \log 2$$

A plot of $\log c[\mathrm{OH}]_S$ against $\log c[\mathrm{OH}]_P$ gives a straight line (Fig. 2), in which $k_S/k_P = 0.17$ (or 1/5.8). Therefore, $c[\mathrm{OH}]_S = 2c[\mathrm{OH}]_P^{0.17}$.

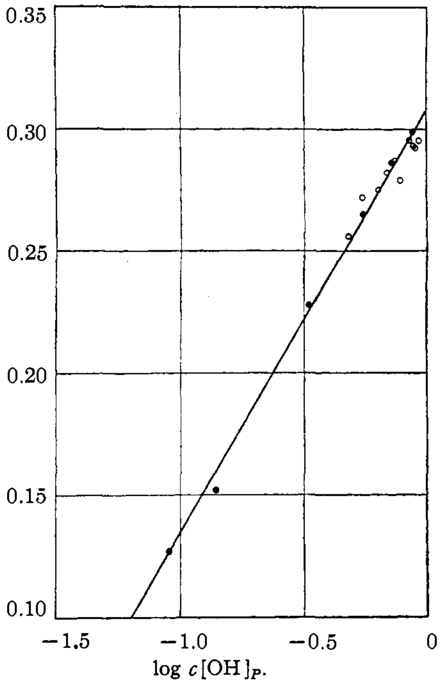

Fig. 2.—Relation between free primary and free secondary hydroxyl groups of tosylated cellulose: ○, series A; ●, series B.

In this heterogeneous esterification, under the conditions used, the relative rates of reaction are such that it is not possible to substitute primary hydroxyls with tosyl groups without also replacing an appreciable number of secondary hydroxyl groups.

Moreover, the data do not permit the detection of a difference in the rate of reaction between the two secondary hydroxyl groups (position 2 and position 3 in the anhydroglucose unit) as previously found for the *homogeneous* tosylation of partially substituted cellulose derivatives.[5-6]

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Summary

1. A chemically reactive cellulose was prepared by regeneration from cellulose xanthate solution, replacing the water in the swollen structure successively with methanol, ethyl ether, and cyclohexane.
2. Two series of heterogeneous esterifications with tosyl chloride in pyridine were made on two such cellulose samples.
3. The products were treated with sodium iodide in acetonylacetone to replace the tosyl groups on primary alcoholic positions by iodine.
4. From the data, the reaction for both primary and secondary alcoholic groups of cellulose was proportional to the concentration of such groups, the rate constant for substitution on the primary position being 5.8 times that for the secondary position.

APPLETON, WIS. RECEIVED JULY 21, 1949

[A CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ARKANSAS]

The Alkaline Hydrolysis of Ethyl Acetate in Acetone–Water Mixtures

BY EDWARD S. AMIS AND SAUL SIEGEL

Potts and Amis[1] studied the rate of the alkaline hydrolysis of ethyl acetate in ethyl alcohol–water mixtures. They found a normal effect for an ion–dipolar molecule reaction with respect to ionic strength effect, but with respect to the effect of dielectric constant of the media, the rate while changing in the direction expected was abnormally influenced by the dielectric constant of the media. It was hoped that a study of the reaction rate in a different medium might show whether this abnormal effect was specific to the ethyl alcohol–water solvents or whether the reaction was abnormally affected in the case of the different media by the dielectric constant. It was decided to choose a non-hydroxylic solvent and at the same time one which gave with water mixtures of known dielectric constants. Acetone was the solvent chosen and the following is a report of the results obtained.

Experimental

To obtain media of different dielectric constants, acetone and water were mixed in various proportions as given by the data of Akerlof.[2] The acetone was prepared according to the procedure of Akerlof, as follows. Acetone, J. T. Baker Analyzed, was treated in batches of about three liters with a small amount of 85% phosphoric acid and immediately distilled. Then it was dried with burnt powdered lime for a day, poured off and redistilled, rejecting all but the fraction which came over between 55.5 and 56.0°. The C. P. ethyl acetate, Eimer and Amend, is manufactured in a high state of purity and therefore, the reagent was simply dried over burnt lime for twenty-four hours and distilled; the fraction boiling between 75.9 and 76.0° was collected. The product was tested by checking a kinetic run whose reaction rate constant has been well established.

Freshly boiled distilled water was always used in preparing aqueous solutions. Carbonate-free sodium hydroxide stock solutions were prepared.[1] The concentrated solution was then diluted to approximately 0.2 *N* and stored in a paraffin-lined carboy. From this stock solution was prepared the 0.1000 and 0.0200 *N* solutions actually used in the runs.

The hydrochloric acid stock solution was prepared by diluting C. P. concentrated (37%) acid and titrating against sodium carbonate. Then, the 0.0200 *N* hydrochloric acid used in the titration was prepared as needed by dilution of the stock solution.

All volumetric apparatus and weights were calibrated for accuracy and the thermometer was calibrated against a Bureau of Standards thermometer.

The rate of ester hydrolysis was studied at 0.00, 15.87 and 26.10° and duplicate runs were performed in every case.

To test the ionic strength dependence, the dielectric constant was held constant at 75.25 and kinetic runs were made at the three temperatures mentioned above for μ-values of 0.02, 0.05, 0.10, 0.20 and 0.30. In the case of dielectric dependence μ was held at a value of 0.02 and dielectric constant varied as given in Table III.

The procedure in following the course of the reaction between ethyl acetate and sodium hydroxide was that described by Potts and Amis.[1] Samples were removed and titrated at suitable intervals during the first 80% of the reaction after which the flasks were kept at room temperature (approximately 25°) for about forty-eight hours. A final titration after two days determined the value of C_∞.

The reaction velocity constant, k', was calculated using the equation

$$k' = \frac{2.303}{tC_\infty} \log \frac{C_n(C_i - C_\infty)}{C_i(C_n - C_\infty)} \qquad (1)$$

where

t = time elapsed in minutes
C_i = NaOH concentration at t_i
C_n = NaOH concentration at t_n and
C_∞ = NaOH concentration at the completion of the reaction

The derivation of this equation is given by Reicher.[3] The time, t_0, of mixing was not observed since the actual concentration of reactants at an initial time, t_i, was determined after mixing by the same analytical means used

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(1) Potts, Dissertation, Louisiana State University, 1948; Potts and Amis, THIS JOURNAL, **71**, 2112 (1949).

(2) Akerlof, *ibid.*, **54**, 4125 (1932).

(3) Reicher, *Ann.*, **228**, 257 (1883).