TABLE II

EFFECT OF STIRRING SPEED

Stirring speed, r. p. m.	Stirring heat, $h_1/C\omega_1$, °C.	$\Delta H/C$
550	0.0028	13.22
800	.0077	13.16
990	.0167	13.21
1125	.0182	13.18
1250	.0249	13.17

In most of the runs of this work a stirring speed of about 1000 r. p. m. was used, with occasional higher speeds at fast flow rates or lower speeds in slow runs, since in addition to sufficient stirring, a minimum stirring heat was desirable.

Summary

By the study of the temperature rise in a stirred flow reactor, a method has been developed which yields accurate rate constants and heats of reaction for quite rapid reactions. The rate and heat of saponification of ethyl α-hydroxyisobutyrate in aqueous solution has been determined under conditions for which the reaction half-time was as little as seventy seconds, and the temperature rise as little as 0.3°. The results are in excellent agreement with other precision determinations of this rate. The method distinguishes between first and second order kinetics, and does not depend upon any analytical determination of the product or reactant concentrations.

Heat leak, stirring and mixing corrections which must be applied to the observed steady state temperature rise are discussed and the method for their evaluation given.

Thermistor resistance thermometers have been used in a balanced Wheatstone bridge to measure fractions of a degree to 0.1% or better.

A device has been described which both maintains constant liquid flow and measures the flow by displacement.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, AND FROM THE DEPARTMENT OF COLLOID SCIENCE, UNIVERSITY OF CAMBRIDGE, ENGLAND]

The Topochemical Alkaline Hydrolysis of Cellulose Acetates. I. The Kinetics of Alkaline Hydrolysis of Sugar Derivatives

BY BERNARD RABINOVITCH*,[1] AND A. E. ALEXANDER[1a]

Introduction

The reactivity of a swollen cellulose derivative in a chemical exchange depends essentially on its physical condition in the swollen phase, since, other things being equal, this will determine the accessibility of the reaction sites in the polymer chain to the reacting ion or molecule.

Two limiting cases may be considered. In the first, the polymer phase is so highly swollen that the diffusion rate of the reacting ion or molecule to the reaction sites, and of the reaction products away from there, is very much greater than the rate of the chemical exchange.[2] Here, this latter rate is the over-all rate-determining process and gives rise to a "topochemical permutoid reaction" in which the kinetics of homogeneous reactions in solution hold.[3]

In the second case, the polymer phase maintains sufficient of its physical structure in the dry state to slow down the rate of the diffusion process much below that of the chemical reaction. Here, diffusion is the rate-determining step in the over-all reaction, giving rise to "topochemical heterogeneous" conditions, and consequently we must introduce into the kinetic equation a linear diffusion coefficient in order to describe it completely.[4]

When a cellulose acetate is saponified in a topochemical permutoid system, the kinetics of the reaction are complicated by the existence in the polymer molecule of reaction sites of different reactivity, characteristic of primary (6-position) and secondary (2- and 3-positions) ester groups, besides possible steric effects introduced through interference of adjacent acetate groups in the secondary positions. In the topochemical heterogeneous reaction, differences in reactivity in the same chain arise because of the different degrees of swelling attained by the amorphous and the crystalline regions of the cellulose acetate. In fact, we may expect to find, between these two limiting cases, a range of conditions in which a polymer chain, or a part of one, reacts under permutoid conditions at one time during the reaction and heterogeneously at another.

In this paper, we shall concern ourselves with investigating the alkaline hydrolysis, under homogeneous conditions, of sugar esters simpler than, but chemically similar to, cellulose acetate. In this way we may study the difference in reactivity arising solely from the chemical characteristics

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(2) R. Taft and L. E. Malm, *J. Phys. Chem.*, **43**, 499 (1939); J. J. Bikerman, *ibid.*, **46**, 724 (1942).

(3) Kurt Hess and C. Trogus, *Z. physik. Chem.*, **B15**, 157 (1931).

(4) K. Atsuki and M. Ishiwara, *Proc. Imp. Acad., Japan*, **4**, 382 (1928).

of the primary and secondary groups in the anhydro-pyranose ring. Purves and his collaborators[5] have studied a similar problem with a view to elucidating the distribution of substituents along the chain in ethyl cellulose and cellulose acetate. Their results indicate that the reactivity of the 6-, 2- and 3-positions in the anhydroglucose ring toward tosylation lie in the ratio 23:2.2:0.11 for cellulose acetate, and that, of the total number of free hydroxyl groups present in the commercial cellulose acetate, about one-half are in the 6-position. In the etherification of a colloid-dispersed cellulose, however, they found that the 6-position reacted at a rate equal to the sum of the rates of the 2- and 3-positions, *i. e.*, not more than a ratio of 2:1. Furthermore, Spurlin[6] has pointed out that the relative amounts of mono-, di- and tri-substituted glucose rings obtained from the hydrolytic breakdown of a partially substituted cellulose ether can be explained on the basis of almost equal reactivity of the three positions, and random distribution of substituents along the chain.

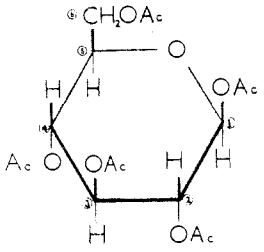

Fig. 1a.—Glucose pentaacetate.

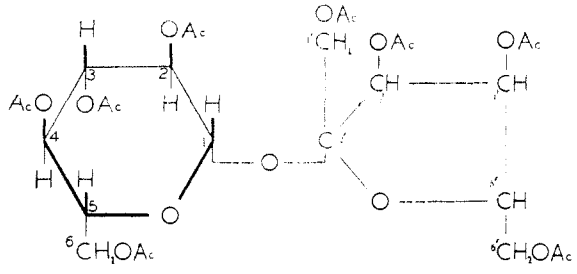

Fig. 1b.—Sucrose octaacetate.

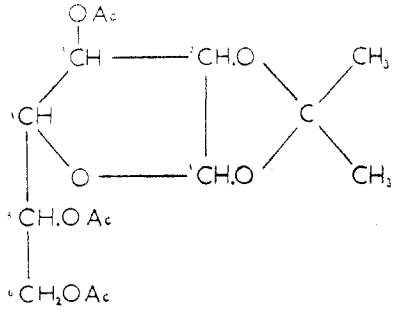

Fig. 1c.—Triacetylmonoacetoneglucose.

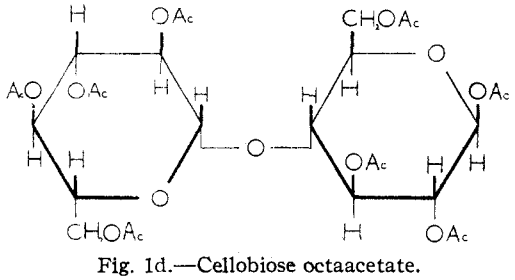

Fig. 1d.—Cellobiose octaacetate.

It seems probable, therefore, that the reactivities of the three positions in the anhydroglucose ring do not differ by more than a factor of 2 in etherification and in acid hydrolysis of ester groups,[7] but when steric effects are probable, as in tosylation, the ratio of reactivities may be as high as 200.

Experimental

Glucose pentaacetate,[8] sucrose octaacetate,[8] cellobiose octaacetate[8] and the triacetyl derivative of monoacetone glucose (Fig. 1) were all tested for purity by hydrolyzing a sample of the sugar ester and estimating its degree of acetylation. This method showed that each compound complied exactly with the requirements for complete acetylation of the sugar.

In addition, the triacetyl monoacetone glucose, which was prepared from monoacetone glucose[8] by the method of Ohle and Spencker,[9] was subjected, after two recrystallizations from low-boiling petroleum ether, to a cryoscopic determination of its molecular weight in benzene. The result gave a value of 373 as compared to a calculated value of 346, *i. e.*, an error of 7%. This was taken as sufficient indication of its purity, in spite of the fact that its m. p. was consistently found to be 60° as compared to 75° given by Ohle and Spencker.[9a]

These sugar esters, when not in use, were kept in stoppered bottles in a vacuum desiccator over calcium chloride.

Method.—All experimental kinetic runs were carried out under second-order conditions at 20° in a mixture of equal volumes of 0.1 *N* standard sodium hydroxide and redistilled commercial acetone. The course of the reaction was followed by determining conductometrically the sodium hydroxide concentration at time intervals. Figure 2 shows the conductivity cell used for this purpose, the resistance of the reaction mixture being measured by means of a Wien bridge. The potential difference across the bridge was 50 volts being supplied at 1000 cycles per second from a beat frequency oscillator, and the balance point obtained by means of a tuned telephone plus amplifier.

Extreme care was necessary to ensure that the platinum black on the electrodes was maintained perfectly clean, and this was done by immersing them in a chromic acid cleaning mixture after every experiment, stripping them clean and replatinizing after every third experiment. In this way, the resistance of the cell containing the hydrolyzing medium could be maintained constant over at least a period of twenty-four hours.

Fifty cubic centimers of the hydrolyzing medium was pipetted into the cell (50 millimoles per liter), an exact quantity of ester, equivalent to 32.5 mmoles. of acetate groups/liter, weighed into a thin-walled glass bulb and placed inside the tubular glass stirrer A. With the stirrer and cell assembled, the whole was allowed to reach equilibrium in a thermostated bath until, with the stirrer rotating, the resistance of the cell remained constant. At this time the glass bulb was broken by raising and lowering the stirrer, and immediately the resistance of the cell was

(5) C. B. Purves, *et al.*, THIS JOURNAL, **61**, 3458 (1939); **64**, 9, 15, 1539 (1942).

(6) H. M. Spurlin, *ibid.*, **61**, 2222 (1939).

(7) The free hydroxyl groups in a commercial acetone-soluble cellulose acetate are produced by acid hydrolysis from the triacetate in solution.

(8) Supplied by Professor W. N. Haworth and Dr. S. Peat, University of Birmingham, England.

(9) H. Ohle and K. Spencker, *Ber.*, **59**, 1845 (1926).

(9a) This difference in m. p.'s could be due to a simple difference in the sugars used, *e. g. d*- and *l*-rotatory.

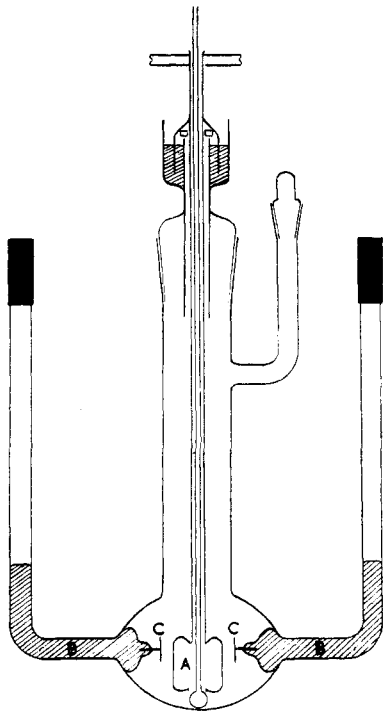

Fig. 2.—Conductivity cell.

taken at suitable time intervals. The convenience of using an exact quantity of ester for every experiment made it possible to check the infinity resistance reading for completion of the reaction. This infinity reading always checked to within three ohms of the calculated value of the resistance of the cell at the completion of the reaction. Even after twelve hours from completion, any change in the resistance of the reaction mixture could readily be accounted for by the contamination of the electrodes and such experiments were rejected. This check served to indicate that no hydrolytic breakdown of the regenerated sugars was taking place.

Resistance–Concentration Relation.—In order to translate resistance readings into concentrations of sodium hydroxide, a calibration curve of resistance of cell *versus* concentration of sodium hydroxide was determined using solutions of varying hydroxide and acetate ion concentrations and constant sodium ion concentration (50 moles/liter) in the acetone water medium. Such a curve could be fitted very well by the relation

$$\text{Resistance of cell} = R = \frac{l/A}{C_{OH}(\Lambda_\infty^{OH} - \Lambda_\infty^{Ac}) + C_{Na}(\Lambda_\infty^{Ac} + {}_\infty{}^a) - a\{C_{OH}^{4/3} + C_{Na}^{4/3} + (C_{Na} - C_{OH})^{4/3}\}}$$

where C and Λ_∞ are, respectively, the concentrations and equivalent conductivities at infinite dilution of the hydroxyl, acetate and sodium ions; l is the distance apart of the electrodes of area A. Since the last term in the denominator remains sensibly constant, varying over this concentration range by only 2.5%, this expression[10] may be rewritten $R = X/(c_{OH} + Y)$ where X and Y are constants. Figure 3 shows the agreement between the experimental curve and theory for two temperatures.

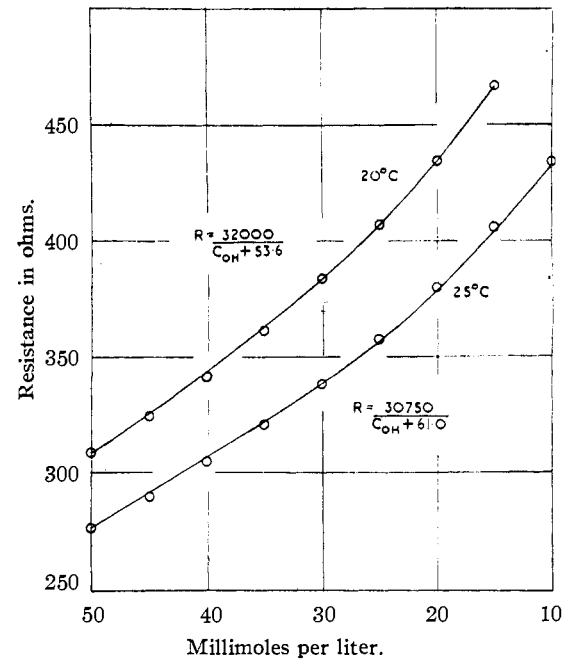

Fig. 3.—Resistance of cell *vs.* concentration: curve, experimental; points, theory.

Analysis of Data

In order that the data obtained from the hydrolysis of a sugar acetate in solution may be used to give values for the rate constants and the concentrations of the different types of ester groups, certain assumptions must be made.

Firstly, it must be assumed that the ester groups around the gluco-pyranose ring react independently one from the other, so that in one and the same molecule chemical exchange can take place simultaneously at two or more reaction sites. That this assumption is justifiable can be seen if we consider that an acetate group in the 6-position is of the order of 9 Å. removed from both the 2- and 3-positions, whilst it is at least three carbon atoms away from the nearest acetate group in the same ring. Moreover, in the sugar esters under examination, the acetate groups on adjacent carbon atoms are *trans* to one another. We can therefore expect, as Spurlin[6] has pointed out, that there will be little or no steric hindrance to the approach of an hydroxyl ion to a reaction site, and that the inductive influence of a substituent in the 6-position on the reactivity of others in the ring will be zero.

We must also assume that the presence or absence of an acetate group at any position in the ring will not affect the reactivity of an acetate group anywhere else in the ring.

In order to justify this assumption, we must

(10) Derived from $\Lambda = \Lambda_\infty - ac^{1/2}$ given by Kohlrausch, "Leitvermogen der Elektrolyte," 1916, p. 107.

examine the analogous case of the hydrolysis of glycol diacetate. J. Meyer[11] found experimentally that in the alkaline hydrolysis of diesters of diacidic alcohols, the velocity constants for the two ester groups lie in the ratio of 2:1. Ingold[12] explained this on purely statistical grounds. However, the existence of this factor 2 says no more than that the glycol diacetate molecule reacts twice as fast as the glycol monoacetate molecule simply because, in an activated collision, the OH^- ion has two chances of reaching a reaction site in the former case, and only one in the latter. On the basis of energetics, however, it is apparent that each acetate group has the same chance of reacting with an OH^- ion whether or not the second acetate group is present, since each presents a similar potential energy barrier to an approaching OH^- ion. This can be adequately shown if the acetate groups are taken as quite independent of each other, so that the unit of concentration is *moles of acetate groups per liter*, and Meyer's data replotted on this basis; we then obtain one velocity constant for the whole reaction to completion and equal to that for glycol monoacetate. We may therefore say that, under similar conditions in the sugar esters, the reactivity of each ester group is independent of the state of substitution of adjacent carbon atoms, and thus of the state of substitution of the ring as a whole.

On the basis of these two assumptions, then, we may compare the sugar ester to a mixture of simpler esters, each with a characteristic velocity constant of hydrolysis. It is apparent that in the hydrolysis of such a mixture, if a plot of $\log_{10} (a - x)/(b - x)$ *vs.* t is made, where a is the concentration of sodium hydroxide initially, b, the concentration of total ester initially ($a > b$) and $(a - x)$, the concentration sodium hydroxide at time t, a curve will be obtained, concave to the t-axis at first and finally linear. The linear portion corresponds to the hydrolysis of the slower reacting ester 2 (initial concentration $= b_2$) in the absence of the faster reaction ester 1 (initial concentration $= b_1$) and its slope $= (a - b)\, k_2/2.303$.

A linear extrapolation to zero time gives an intercept of $\log_{10} (a - b) + b_2/b_2$ and to time t of $\log_{10} (a - b) + (b_2 - x_2)/(b_2 - x_2)$ where $(b_2 - x_2)$ = the concentration of ester 2 at time t. Thus, $(b_1 - x_1)$ and $(b_2 - x_2)$ may be found.

An extrapolation of this sort is only justifiable if the *velocity* of hydrolysis of ester 1 is much greater than that of ester 2, so that little of ester 2 is hydrolzed during the time that the concentration of ester 1 approaches zero. Since the two velocities may be written

$$v_1 = k_1 a b_1 \text{ and } v_2 = k_2 a b_2$$

it is apparent that this condition is fulfilled if either $k_1 \gg k_2$ or $b_1 \gg b_2$. If, however, $k_1 \simeq k_2$ or $b_1 \simeq b_2$, a linear extrapolation is not justifiable and we must resort to a graphical method of successive approximations. This procedure is tedious to carry out, but may be explained as follows:

At time t_c, the point at which ester 1 may be considered to be completely hydrolyzed, we know that our experimental value of $(b - x)$ is equal to $(b_2 - x_2)$. By assuming that over the small but finite time interval Δt immediately prior to t_c the rate of reaction dx_2/dt of ester 2 is the same as that immediately after t_c, we obtain an approximate value for $(b_2 - x_2)$ at time $t_c - \Delta t/2$. We know the value of $(a - x)$ at this time, and from the equation

$$\Delta x_2/\Delta t = k_2\{(a - x)(b_2 - x_2)\}_{t_c - \Delta t/2}$$

we obtain a value for Δx_2, the change in x_2 during the time interval $t_c - \Delta t$ to t_c. This then gives another value for $(b_2 - x_2)$ and we may repeat the process over the time interval $t_c - 2\Delta t$ to $t_c - \Delta t$ by using the value of $(a - x)$ at time $t_c - 3\Delta t/2$ and the approximate value of $(b_2 - x_2)$ at this time.

In this way we obtain a series of values of $(b_2 - x_2)$ at various times from $0 \rightarrow t_c$ which will approach the real values as Δt becomes infinitesimally small (*i. e.*, dt). However, in practice it was found that little was gained in accuracy if Δt was reduced below one half-minute.

Experimental Results

Mixtures of Simple Esters.—A series of preliminary experiments were carried out at 25° on mixtures of the following simple esters: glycol monoacetate, ethyl acetate and isopropyl acetate, in order to test the validity of the above analysis and to compare velocity constants thus obtained with those obtained for the isolated esters. These latter values for the three esters are, respectively, 14.1, 3.65 and 0.68 $mole^{-1}$ $min.^{-1}$ liter. Figures 4 i and ii compare, for these experiments, values of $(b_2 - x_2)$ obtained by a linear extrapolation and by the method of successive approximations. It can be seen in i that when k_1/k_2 increases from 5.4 for the ethyl acetate–isopropyl acetate pair (expt. 64) to 21 for the glycol monoacetate–isopropyl acetate pair (expt. 62), the difference between the two methods approaches zero. Similarly, in ii when k_1/k_2 is kept constant at 3.9, as b_1/b_2 increases from 0.98 to 3.40, again the difference between the two methods tends to disappear.

The results of these preliminary experiments show that under any conditions k_2 can be determined with an accuracy of $\pm 2\%$, whilst if b_1/b_2 is at least 2 and k_1/k_2 not less than 5, then k_1 can be determined with an accuracy of $\pm 5\%$. If these ratios are smaller, the divergency of k_1 is greater.

Sugar Esters.—Glucose pentaacetate, triacetyl monoacetone glucose and sucrose octa-

(11) Julius Meyer, *Z. physik. Chem.*, **67**, 257 (1909).
(12) C. K. Ingold, *J. Chem. Soc.*, 1375 (1930).

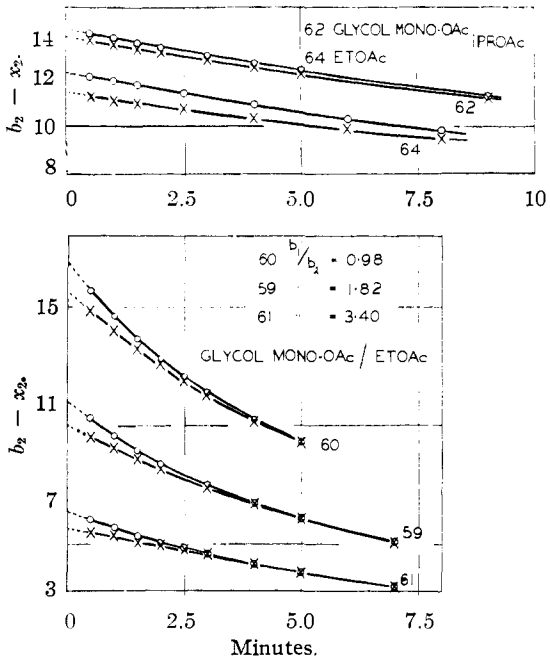

Fig. 4.—Upper, i; lower, ii; O, method of successive approximations; ×, method of extrapolation.

acetate, as well as their respective reaction products, are all soluble in the solvent medium used in all these experiments, so that they react under completely homogeneous conditions throughout. Cellobiose octaacetate, on the other hand, is completely insoluble in water, seems to swell in acetone, and is soluble in chloroform. Because of this difference in solubility, it has been possible to hydrolyze this ester under varying conditions, and to draw conclusions from its significantly different behavior under these conditions.

Figure 5 shows the results of some of these hydrolyses in solution. Here b, b_1 and b_2 are expressed in mmoles. of acetate groups/liter. It is immediately apparent that conditions $k_1 \gg k_2$ and $b_1 \gg b_2$ hold for these experiments, conditions which are most favorable for determining k_1 but least favorable for k_2 and b_2. However, the following facts emerge immediately: the hydrolysis rate constant for the slower reacting ester groups is the same, within experimental error, in all cases; calculated values of b_2 from these curves always lie between 4 and 7 mmoles./liter (in all cases, total ester concentration is 32.5 mmoles./liter).

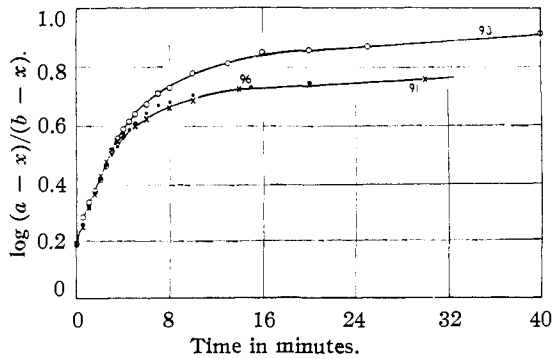

Fig. 5.—Hydrolysis of sugar esters in solution: O, glucose pentaacetate; ×, sucrose octaacetate; ●, triacetylmonoacetoneglucose.

When cellulobiose octaacetate is hydrolyzed in a heterogeneous system, either by presenting it to the hydrolyzing medium as a dry solid or wetted with acetone, remarkably different behavior is observed, as shown in Fig. 6. If the cellobiose octaacetate is, however, previously dissolved in chloroform (0.5 cc.), so that on coming into contact with the hydrolyzing medium it is precipitated out in the presence of OH^- ions, then

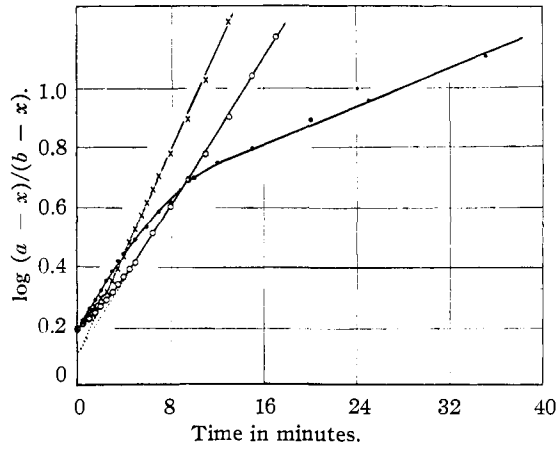

Fig. 6.—Topochemical hydrolysis of cellobiose octaacetate: O, initially dry; ×, initially wetted by acetone; ●, initially in chloroform solution.

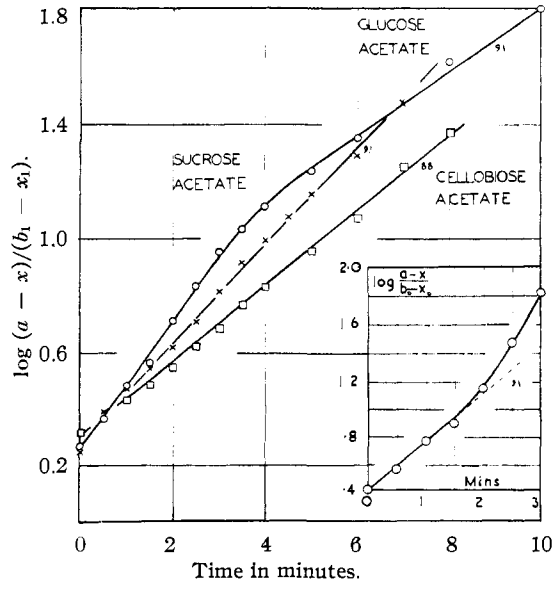

Fig. 7.—Derived curves for ester hydrolysis; inset, second derived curve for sucrose octaacetate.

TABLE I

Sugar ester	Mmoles/liter b	b_1	b_2	Ester groups/sugar molecule b_0	b_1	b_2	Moles^{-1} min.$^{-1}$ liters k_0	k_1	k_2
Glucose, pentaacetate		26.5–28.5	4–6		4	1		17	0.3
Triacetyl monoacetone glucose		25.5	7		2	1		15	0.3
Sucrose octaacetate	17.5–22.5	7–9	4–6	5	2	1	25	12	0.3
Cellulobiose octaacetate		24–25	7.5–8.5		6	2		12	2.4

behavior similar to that shown by the homogeneous systems is observed. This latter reaction can be taken to be a permutoid reaction.

The derived curves, *i. e.*, $\log_{10}(a-x)/(b_1-x_1)$ *vs.* t, can be seen in Fig. 7. For all but sucrose octaacetate straight lines are obtained, corresponding to ester groups of the same reactivity in each molecule, but the sucrose derivative is shown still to be made up of substituents of different reactivity. This cannot be an artifact since a plot of this type for a single ester group will tend to deviate in an upward direction, if at all. Extrapolation of this derived curve to zero time gives a b_2 value for sucrose octaacetate of 7–9 mmoles./liter.

The results of these experiments (with the exception of topochemical heterogeneous reactions of cellobiose octaacetate[13]) are summarized in Table I.

Discussion

It appears that the assumptions involved in the analysis of the above data lead to results which can be interpreted readily in terms of structure. Comparison of the chemical structures shown in Fig. 1 with the third column of Table I shows that in all cases the slower reacting ester groups correspond in number to the primary acetate groups. In the case of sucrose octaacetate, however, the three primary acetate groups seem to be of two kinds, b_1 and b_2, whilst those in, say, cellobiose octaacetate show no such differentiation. The exact interpretation of this fact is in some doubt, as there are two possible ways of distinguishing these ester groups in the sucrose derivative. On the one hand, we may consider the two primary acetate groups in the fructo-furanose (γ-sugar) ring to be more reactive than the one in the gluco-pyranose ring; and on the other hand, we may consider the two groups in the 6- and 6′-positions as equal in reactivity whilst that in the 1′-position as being unique in the molecule.

A similar difficulty arises in assigning a position to the slower reacting ester group in triacetyl monoacetone glucose. Here, again, we are dealing with a γ-sugar, made up of an α-glucofuranose ring with a stable acetone residue in the 1,2-position, and the choice lies between the primary ester group in the 6-position or the secondary ester group in the 3-position, which now has no acetate group on its adjacent carbon atoms.

It is clear, however, in the other cases, that it is, in fact, the secondary ester groups in the ring which are the most reactive in hydrolysis, and since they react at the same rate and faster than the primary ester groups, they must be of the glycolic type. If this is so, then it seems reasonable to suppose that, in triacetylmonoacetone-glucose, those ester groups in the 5- and 6-positions, which are clearly of the glycolic type, hydrolyze most rapidly, even though one of them is of a primary character, whilst that in the 3-position, isolated as it is, is slow to react. We may therefore say that what will determine the reactivity of an acetate group in the sugar ring will be, not whether it is a primary or secondary group, but whether it has an ester group (or free hydroxyl) on an adjacent carbon or not.

It is interesting to note that for those reactions carried out under completely homogeneous conditions, the ratio of velocity constants of the glycolic groups to primary lies between 50 and 80, whereas in the permutoid reaction this ratio decreases to 5. Not enough experiments have been carried out to give an adequate explanation of this phenomenon, but a possible explanation emerges from a consideration of the conditions under which the permutoid reaction was carried out. It is only when the cellobiose octaacetate is precipitated in the presence of OH^- ions that permutoid conditions are attained, and in this way OH^- ions become equally available at all reaction sites. In the case of a homogeneous reaction in solution, the probability of an OH^- ion reaching a primary ester group rather than a glycolic ester group in an activated collision with, say, sucrose octaacetate is of the order of 1/8, with glucose pentaacetate 1/5 and with triacetyl monoacetone glucose 1/3. This is reflected in the ratio of velocity constants which lie in the inverse order, 25/0.3, 17/03, 15/0.3. It therefore seems possible that the increased rate of hydrolysis of the primary ester groups in the permutoid reaction of cellobiose octaacetate is due to the increased availability of OH^- ions at these groups.

In comparing these results with those of Spurlin[6] and of Purves[5] on the acid hydrolysis of cellulose acetate, we find that the relative rates of hydrolysis of the primary and glycolic groups have been reversed in alkaline hydrolysis. However, this may readily be understood since it is frequently found that, in ester hydrolysis, the k_{OH}/k_H ratio for a primary ester is of a different order of magnitude from that for a secondary or glycolic ester.[14] In fact, this ratio for ethyl acetate is 2 and for glycol monoacetate 10,

(13) To be discussed in a later publication.

(14) C. K. Ingold, *J. Chem. Soc.*, 1032 (1930).

which, if one takes cellobiose octaacetate as being typical of a permutoid reaction, make k_1 and k_2 for acid hydrolysis the same and equal to 1.2 moles^{-1} min.$^{-1}$ liters. This seems to be more nearly in accord with these previous authors who say that the rate of hydrolysis of the primary ester group is, at least equal to, and at most twice, that of a glycolic ester group in cellulose acetate.

Summary

The alkaline hydrolysis of sugar acetates in solution may be treated as that of a mixture of simple esters, each with its own characteristic velocity constant. Under these conditions, the primary acetate groups in glucose pentaacetate, triacetyl monoacetone glucose and sucrose octaacetate react at a slower rate than the secondary groups which have been shown to be glycolic in nature. In the case of sucrose octaacetate, the primary groups are made up to two types reacting at different rates.

In the case of cellobiose octaacetate, the hydrolysis can be carried out under permutoid conditions by precipitating the ester from chloroform solution in the presence of OH^- ions, when it behaves in a similar fashion to glucose pentaacetate. Under other heterogeneous conditions it behaves in a radically different manner.

CAMBRIDGE, MASSACHUSETTS
CAMBRIDGE, ENGLAND RECEIVED SEPTEMBER 6, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Kinetic Studies on the Decarboxylation of Sodium Trifluoroacetate in Ethylene Glycol

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Sodium trifluoroacetate, like the salts of other halogenated acetic acids, undergoes thermal decomposition in the solid state, photochemical decomposition, hydrolysis and decarboxylation. This paper reports studies on the rate of the decarboxylation reaction, for comparison with the data on the decarboxylation of sodium trichloroacetate.[2]

Initial attempts to decarboxylate sodium trifluoroacetate or trifluoroacetic acid in solvents in which trichloroacetic acid and its salts decomposed were without success. Neither the salt nor the free acid decomposed in water, ethyl alcohol or pyridine at temperatures below the boiling points of the solvents, nor in aniline or *m*-cresol up to 138°. Decarboxylation of the sodium salt did occur at a conveniently measurable rate in ethylene glycol at temperatures near 180°, and the reaction was studied in this solvent. Since side reactions occurred if the solution was allowed to become basic, many of the experiments were carried out in the presence of boric acid. For comparison, a few experiments were made with sodium trichloroacetate.

Sodium trifluoroacetate from Columbia Organic Chemicals was dissolved in ethyl alcohol and thrown out by adding dioxane. The resulting solid was recrystallized four times from hot absolute alcohol and dried at 120–130° at 1 mm. pressure. Analysis gave 16.65% sodium (theoretical, 16.88%).

Sodium trichloroacetate was prepared according to the directions of Hall and Verhoek.[2b]

Ethylene glycol was dried over Drierite for several days, decanted, and distilled at a pressure of 2 mm. through an 18-inch column packed with multiple-turn quarter-inch helices. The first 10% of the constant boiling fraction was discarded and the remainder of the distillate collected and stored in nitrogen-filled glass-stoppered bottles.

The reacting solutions were prepared with precautions to exclude moisture, two 10-ml. samples removed, and the remainder sealed in a reaction flask and placed in the thermostat. The reaction flask had a capillary tube extending from the bottom up over the side of the thermostat, and ending with a stop-cock. The pressure of hot air and vapor in the flask forced a sample out when the stop-cock was opened. About 1 ml. of solution was discarded before each sample was taken, to remove any material which might have been in the capillary (volume 0.5 ml.) at a lower temperature than the bath. A sample of about 10 ml. was then collected, weighed, swept with nitrogen for ten minutes to remove carbon dioxide and titrated for the amount of base formed or boric acid left. The results were converted to volume concentrations using the measured densities of the solutions. The reaction was considered complete when two samples removed several hours apart showed the same titer. The difference between the initial and final values, compared to the weight of salt originally taken, gave the per cent. of the salt which underwent decarboxylation.

The products of the decarboxylation of trifluoroacetic acid would be expected to contain equimolar quantities of the two gases carbon dioxide and fluoroform. Analysis of the gas evolved on decomposing sodium trifluoroacetate dissolved in ethylene glycol showed only 24% carbon dioxide, however, due to retention of this gas by the basic solution formed. When boric acid was present in the solution, three separate experiments at 173° gave 51, 50 and 50% of the evolved gas absorbed in 30% potassium hydroxide, indicating that the over-all reaction was

$$CF_3COO^- + H^+ \longrightarrow CHF_3 + CO_2$$

A solution of boric acid and ethylene glycol heated alone produced no gas.

The decarboxylation reaction was found to be of the first order throughout the course of each individual reaction, as shown by the fact that

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(2) (a) Verhoek, THIS JOURNAL, **56**, 571 (1934); (b) Hall and Verhoek, *ibid.*, **69**, 613 (1947); (c) Fairclough, *J. Chem. Soc.*, 1186 (1938).