

ART. XXXII.—*On the Preparation and Hydrolysis of Esters Derived from the Substituted Aliphatic Alcohols*; by W. A. DRUSHEL and G. R. BANCROFT.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxciii.]

IN 1894 de Hemptinne,* working under the direction of Van't Hoff, determined the velocity constants for the hydrolysis of eleven of the lower aliphatic esters. These included methyl, ethyl, propyl acetates, propionates, butyrates, also ethyl isobutyrate and ethyl valerate. This work of de Hemptinne showed that the unsubstituted alcohol radical has very little influence upon the rate of acid hydrolysis. Later in the same year Löwenherz,† also under Van't Hoff, determined the velocity constants for the acetates of glycerol and phenol. By a comparison of these results with those obtained by de Hemptinne for methyl, ethyl, and propyl acetates, it was shown that although the alcohol radical has little influence in determining the rate of hydrolysis its chemical nature is of considerable importance.

In 1897 and 1898 Geitel‡ studied the velocities of the hydrolysis of mono-, di-, and triacetates of glycerol when catalyzed with decinormal hydrochloric acid at 25° and found them to be in the ratios of 1:2:3. In 1907 Julius Meyer§ investigated the reaction velocity of the hydrolysis of ethylene glycol monoacetate and diacetate, working at 25.2° and catalyzing the reaction with N/50 and N/100 hydrochloric acid.

The reaction with the glycol diacetate was found to proceed in two stages, the monoacetate being formed as an intermediate product, and this finally decomposing forms ethylene glycol. The rate of hydrolysis in the first stage was determined to be double that of the second stage. E. Abel|| and R. Kremann¶ also have studied the acid and alkaline hydrolysis of esters of the polyhydric alcohols. Their results seem to agree with those of Geitel in that they found the rate of hydrolysis in the case of tri-, di-, and monoacetates of glycerol to be in the ratio of 3:2:1.

In 1910 a study of the effect of constitution on the rate of ester hydrolysis was begun in Kent Chemical Laboratory of Yale University. A series of articles** dealing with the hydrolysis of esters of substituted aliphatic acids has already appeared. In this paper, and others which may follow, the investigation is concerned with the study of the effect of sub-

* de Hemptinne, *Zeitschr. phys. Chem.*, xiii, 561, 1894.

† Löwenherz, *Zeitschr. phys. Chem.*, xv, 389, 1894.

‡ Geitel, *J. pr. Chem.* (2), lv, 417-429, 1897. *Ibid.* (2), lvii, 113-131, 1898.

§ Meyer, *Zeitschr. Elektrochem.*, xiii, 186, 1907.

|| Abel, *Zeitschr. phys. Chem.*, lvi, 558, 1906.

¶ Kremann, *Zeitschr. Elektrochem.*, xiii, 307, 1907.

** Drushel and Hill, *this Journal*, xxx, 72-78, 1910.

stitution in the alkyl radical of an ester upon the rate of hydrolytic cleavage.

Preparation of Materials.

The α -chlor-ethyl acetate was prepared by the method of Simpson,* by heating equimolecular quantities of acetyl chloride and water-free acetaldehyde in a sealed tube at 100°. The ester, boiling at 120°–124°, was purified by fractionation. As a further criterion of purity it was analyzed for halogen. Weighed portions of the ester were hydrolyzed with sodium hydroxide on a steam-bath. The formation of aldehyde resin indicated the presence of acetaldehyde. After filtering off and carefully washing the resin, the filtrate was neutralized with nitric acid and the halogen estimated by titrating with decinormal silver nitrate, using potassium chromate as an indicator.

Chlorine found—I. 28.27%, II. 28.62%.

Chlorine calculated—28.94%.

The α -chlor-ethyl propionate was prepared by the method of Rubencamp.† Equimolecular portions of water-free acetaldehyde and propionyl chloride were heated in a sealed tube at 120°. The ester, boiling at 134°–136°, was purified by fractionation and its halogen content was shown to correspond to theory using the method outlined above for the α -chlor-ethyl acetate. Here, as in the preceding case, aldehyde resin was formed in the hydrolysis.

The α -ethoxy-ethyl acetate was obtained‡ by heating equimolecular portions of the diethyl acetal of acetaldehyde and acetic anhydride in a sealed tube at 150°. The reaction product was washed with a solution of potassium carbonate, then separated and dried over freshly fused potassium carbonate. That portion distilling over at 125°–130° was collected as the pure ester. The acetal from the above preparation was prepared by the method of Fischer and Giebe.§

As a preliminary to the preparation of the β substituted esters the following compounds were prepared in considerable quantity: ethylene dibromide, ethylene glycol diacetate, and ethylene glycol. The ethylene dibromide was prepared by the method of Balard.|| The ethylene glycol diacetate was obtained by refluxing a mixture of one mole of ethylene dibromide with two moles of fused anhydrous potassium acetate in the presence of a mole of glacial acetic acid.¶ A second method**

* Simpson, Compt. rend., xlvii, 874, 1858. Ann. d. Chem. u. Pharm., cix, 156, 1859.

† Rubencamp, Ann. d. Chem., ccv, 276, 1884.

‡ Claisen, Ber. d. d. Chem. Gesell., xxxi, 1018, 1898.

§ Fischer and Giebe, *ibid.*, xxx, 3053, 1897.

|| Balard, Ann. d. chim. et d. Phys. (2), xxxii, 375, 1826. Erlenmeyer and Bunte, Ann. d. Chem. u. Pharm., clxviii, 64, 1873.

¶ Gattermann, Prac. Methods of Org. Chem. 3d ed., p. 196, 1915.

** Henry, Ann. d. chim. et d. Phys. (4), xxvii, 250, 1872.

was also used in the preparation of the glycol diacetate. One mole of ethylene dibromide and two moles of freshly fused potassium acetate were refluxed in a solution of eighty-five per cent alcohol on a water bath for eighteen to twenty hours, and filtered to remove the potassium bromide. The filtrate was fractionated to remove the alcohol and the glycol diacetate was collected at 185°–187°.

The ethylene glycol was produced by the hydrolysis of ethylene glycol diacetate according to the method of Haller,* the process being carried out as described by Louis Henry,† and the yields corresponded to those given by Gattermann.‡

β -Hydroxy-ethyl acetate was first prepared by Atkinson§ by heating on a boiling water bath for two days equimolecular quantities of ethylene dibromide and potassium acetate in a solution of eighty-five per cent ethyl alcohol. De Mole|| claimed a considerable yield of the monacetin of ethylene glycol by heating for eighteen hours at the boiling temperature an equimolecular mixture of ethylene dibromide and freshly fused potassium acetate in an eighty to eighty-five per cent solution of ethyl alcohol. Lourenço¶ obtained this ester by heating equimolecular quantities of ethylene glycol and glacial acetic acid for one day in a sealed tube at 200°.

The above method of Atkinson and De Mole was employed with the hope of obtaining the β -hydroxy-ethyl acetate. Three hundred grams of ethylene dibromide were treated with 155 grams of water-free potassium acetate in 300 grams of 85 per cent ethyl alcohol. This mixture was digested for twenty hours in a flask fitted with a reflux condenser on a boiling water bath. The potassium bromide which precipitated was filtered off, and the filtrate fractionated to remove the alcohol. A yield of 83 grams of diacetate was obtained, but no monacetin was formed, as no reaction took place on treatment of a portion with acetyl chloride.

On treating 300 grams of ethylene dibromide with 310 grams of anhydrous potassium acetate in 300 grams of 85 per cent ethyl alcohol, digesting for twenty-four hours, filtering, and fractionating the filtrate, a yield of 174 grams of glycol diacetate was obtained. This result is in accordance with the experience of Louis Henry,** who states that the diacetate is obtained by treating ethylene dibromide with fused potassium acetate, as described above. This method was tried repeatedly,

* Haller, *Compt. rend.*, cxliii, 657, 1906.

† Henry, *Bull. Acad. Roy. Belg. cl. sci.* (3), xxxii, 402–417, 1896.

‡ Gattermann, *Prac. Methods of Org. Chem.* 3d ed., pp. 197–198, 1915.

§ Atkinson, *Ann. d. Chem. u. Pharm.*, cix, 232, 1859.

|| De Mole, *Ber. d. d. Chem. Gesell.*, vii, 641, 1874. *Ann. d. Chem. u. Pharm.* clxxiii, 117, 1874; clxxvii, 147, 1875.

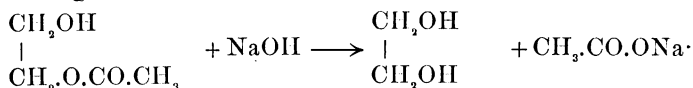
¶ Lourenço, *Compt. rend.*, 1, 91, 1860. *Ann. d. Chem. u. Pharm.*, cxiv, 122, 1860.

** Henry, *Ann. d. chim. et d. Phys.* (4), xxvii, 250, 1872. *Rec. d. trav. chim. d. Pays-Bas*, xx, 243–254, 1901. *Bull. Acad. Roy. Belg. cl. sci.* (3), xxxvii, 236–248, 1901.

always with the same result, and the product was used in the preparation of ethylene glycol. Also on saturating a portion of the product with dry hydrobromic acid gas the β -brom-ethyl acetate was formed.

Finally, a direct esterification method was devised for the preparation of the β -hydroxy ethyl acetate, which is really a modification of that given by Lourenço,* to which reference has already been made. Equimolecular portions of ethylene glycol and glacial acetic acid were digested over twice the theoretical quantity of anhydrous copper sulphate in a flask over a free flame for eight hours. In order to keep track of the esterification, one cubic centimeter of the reaction mixture was pipetted into a graduated flask before heating and the volume made up to 250^{cm}³. Aliquot portions of fifty cubic centimeters were withdrawn and titrated with decinormal sodium hydroxide. Other portions of the reaction mixture were withdrawn from time to time and treated as described above. At the end of eight hours the titration showed that the esterification was practically complete. The esterified mixture was cooled and decanted, and the copper sulphate residue was extracted with ether. The mixture was then fractionally distilled, the main portion coming over at 185°–190°, and on refractionating boiled at 187°–189°. This portion reacted vigorously with acetyl chloride, effervescing briskly with evolution of hydrochloric acid gas.

Weighed portions of this ester were placed in flasks and saponified with an excess of decinormal sodium hydroxide, according to the following equation :



The excess of sodium hydroxide was then titrated with decinormal hydrochloric acid using phenolphthalein as an indicator. From results obtained the ester was shown to be 99.38 per cent pure.

The use of anhydrous copper sulphate as a dehydrating agent† in the esterification of certain hydroxy-acids has been previously described in the literature. In the present investigation this dehydrating agent is used for the first time in the esterification of polyhydric alcohols.

Another point worthy of mention in connection with the preparation of this compound is the low boiling point given by the various investigators. Atkinson gives 182°, De Mole 180°–182°, and Lourenço 180°, as the boiling point of their

* Loc. cit.

† Bogojawlensky and Narbut, Ber. d. d. Chem. Gesell., xxxviii, 3344, 1895. Clemmenson and Heitman, Amer. Chem. J., xlii, 319, 1909. Dean, this Journal, xxxvii, 332, 1914. Drushel, *ibid.*, xxxix, 114–117, 1915.

respective products. Glycol diacetate boils at 186°–187° and ethylene glycol at 197°. From the molecular constitution of the monacetin of ethylene glycol we would naturally expect its boiling point to lie between those of ethylene glycol and glycol diacetate. The boiling point of the main portion of the product obtained by direct esterification was distinctly higher than that given in the literature, and lies between that of the glycol and of the diacetate.

The β -methoxy-ethyl acetate was prepared by treating the β -methoxy-ethyl alcohol with the theoretical quantity of acetyl chloride. The ester, boiling at 144°–145°, was purified by fractional distillation. This ester has been previously prepared* by treating the corresponding alcohol with acetic anhydride.

The β -methoxy-ethyl alcohol was obtained for the preparation of the β -methoxy-ethyl acetate by preparing monosodium glycolate, and treating it with the theoretical quantity of methyl iodide under suitable conditions according to the method of Palomaa.† A separation of the glycol-ether, boiling at 124°–126°, was effected by fractionation.

The β -ethoxy-ethyl acetate was prepared by treating β -ethoxy-ethyl alcohol with acetyl chloride. The excess of acetyl chloride was removed by fractional distillation, and the ester was found to boil at 157°–158°. The alcohol used in this preparation was obtained by the method of Palomaa. The monosodium glycolate was treated with ethyl iodide as described in this method. Upon fractionation the alcohol distilled over at 134°–135°, and possessed the properties given by Palomaa‡ and De Mole.§

The β -ethoxy-ethyl alcohol was also obtained by a second method which is not recorded in the literature, and appears here for the first time. In attempting to prepare β -ethoxy-ethyl acetate by refluxing equimolecular quantities of β -brom-ethyl acetate and sodium ethylate, it was found that β -ethoxy-ethyl alcohol was obtained. The materials were refluxed in a water-free alcoholic solution for half an hour on a water bath. On filtering from sodium bromide and fractionating the reaction mixture, a product was obtained which had all the physical characters of the β -ethoxy-ethyl alcohol. It also reacted with acetyl chloride giving the β -ethoxy-ethyl acetate.

The β -chlor-ethyl acetate was prepared by treating ethylene chlorhydrin with acetyl chloride|| in slight excess of the theoretical amount. The pure ester, boiling at 143°–145°, was obtained by fractionation. The β -ethylene chlorhydrin for the preparation of this ester was obtained according to the method

* Palomaa, Ber. d. d. Chem. Gesell., xxxv, 3300, 1902.

† Palomaa, ibid., xlii, 3873, 1909.

‡ Palomaa, ibid., xlii, 3876, 1909.

§ De Mole, ibid., ix, 745, 1876.

|| Henry, Ber. d. d. Chem. Gesell., vii, 70, 1874.

of Ladenburg.* This ester was analyzed for halogen as a further test of the purity of the substance.

Chlorine found, I. 28.40%, II. 28.18%, III. 28.34%.

Chlorine calculated, 28.94%.

The β -brom-ethyl acetate was obtained by the method of Louis Henry,† which is essentially the same as that described by De Mole,‡ who treated his monacetin of ethylene glycol with hydrobromic acid to obtain this ester. Ethylene glycol diacetate was saturated with dry hydrobromic acid gas, and the resulting product was fractionated. The boiling-point and specific gravity of the purified ester corresponded to the values given in the literature. The halogen content of the ester was also determined by analysis.

Bromide found, I. 47.50%, II. 47.56%, III. 47.50%.

Bromine calculated, 47.86%.

Hydrolysis of Esters.

Esters Derived from Alpha Substituted Ethyl Alcohols.

The following esters of this class were studied :

α -chlor-ethyl acetate, $\text{CH}_3\text{CHCl.O.CO.CH}_3$.

α -ethoxy-ethyl acetate, $\text{CH}_3\text{CH(OC}_2\text{H}_5\text{).O.CO.CH}_3$.

α -chlor-ethyl propionate, $\text{CH}_3\text{CHCl.O.CO.CH}_2\text{CH}_3$.

These esters are found to be unstable compounds, which are decomposed immediately upon dissolving in decinormal hydrochloric acid. This was shown by dissolving 2.5 cm³ of the α -chlor-ethyl acetate in 250 cm³ of the standard decinormal hydrochloric acid. On titrating 25 cm³ of this reaction mixture with decinormal sodium hydroxide, the initial titration required considerably over 45 cm³, and the titration made after allowing the reaction mixture to remain in the thermostat for ten days showed an increase of only one to two cubic centimeters. This increase was accounted for by the more complete splitting out of halogen, which was shown by titrating with silver nitrate.

In the case of the α -chlor-ethyl acetate the hydrolysis products were acetaldehyde, acetic acid and hydrochloric acid, while the α -chlor-ethyl propionate gave acetaldehyde, propionic acid, and hydrochloric acid. The α -ethoxy-ethyl acetate gave a similar result yielding acetaldehyde, ethyl alcohol and acetic acid. The presence of the aldehyde was shown in each case by treating a portion of Schiff's reagent with a few drops of the solution of the hydrolyzed ester, which at once imparted a deep reddish violet color to the solution.

* Ladenburg, *ibid.*, xvi, 1407-1408, 1883. *Jahresb.* 1883, 591.

† Henry, *Rec. d. trav. chim. d. Pays-Bas*, xxi, 243-254, 1901. *Bull. Acad. Roy. Belg. cl. sci.* (3), xxxvii, 236-248, 1901.

‡ De Mole, *Ann. d. Chem.*, clxxii, 121, 1874.

In alkaline solution the reaction was similar to that described above, and the presence of the aldehyde was shown by warming the solution of hydrolysis products on the steam bath, when there was formed the characteristic aldehyde resin of acetaldehyde.

Esters Derived from Beta Substituted Ethyl Alcohols.

The following esters of this class were studied :

β -hydroxy-ethyl acetate, $\text{CH}_3(\text{OH})\text{CH}_2\text{O.CO.CH}_3$,
 β -methoxy-ethyl acetate, $\text{CH}_3(\text{OCH}_3)\text{CH}_2\text{O.CO.CH}_3$,
 β -ethoxy-ethyl acetate, $\text{CH}_3(\text{OC}_2\text{H}_5)\text{CH}_2\text{O.CO.CH}_3$,
 β -chlor-ethyl acetate, $\text{CH}_2\text{Cl.CH}_2\text{O.CO.CH}_3$,
 β -brom-ethyl acetate, $\text{CH}_2\text{Br.CH}_2\text{O.CO.CH}_3$.

These esters were hydrolyzed in decinormal hydrochloric acid at 25°, 35°, and 45°, and measurements made from which the velocity constants were calculated. The hydrochloric acid used as a catalyzing agent was standardized by precipitation with silver nitrate. The titrations were made with decinormal sodium hydroxide, free from carbon dioxide, using phenolphthalein as an indicator.

The hydroxy-, methoxy-, and ethoxy-ethyl acetates were found to be very soluble in water. The introduction of halogen in the β -position of the ethyl radical of the alcohol gives to the derived ester a much greater insolubility. Only eight cubic centimeters of the β -brom-ethyl acetate could be dissolved in a liter of water. The β -chlor-ethyl acetate was found to be slightly more soluble.

In the case of the hydroxy-, methoxy-, and ethoxy-ethyl acetates 2.5 cm³ of each ester were dissolved in 250 cm³ decinormal hydrochloric acid, previously warmed in the thermostat to the required temperature. As soon as the ester was completely dissolved a 25 cm³ portion of the reaction mixture was withdrawn by means of a pipette, and run into about one hundred cubic centimeters of cold distilled water in a 300 cm³ flask. The pipette was allowed to drain thirty seconds and the time was then recorded, and the solution titrated at once with decinormal sodium hydroxide. Subsequent titrations were made at suitable time intervals, and the final measurements were taken when a sufficient time had elapsed to insure that the hydrolytic action was complete. To insure uniformity in experimental conditions a sample of ethyl acetate was hydrolyzed at the same time as the esters of this group, and the hydrolysis of each ester was made in duplicate.

On account of the greater insolubility of the beta halogen substituted esters only two cubic centimeters of each ester were dissolved in 250 cm³ of decinormal hydrochloric acid. Measurements of the velocity of the hydrolysis of these esters were made as just described. In order to ascertain if any halogen was liberated in the form of free halogen acids derived

from the esters, or the halogen substituted alcohols resulting from the hydrolysis of the esters, titrations were made with decinormal silver nitrate at the time when the equilibrium was reached in the titration of the acid with decinormal sodium hydroxide.

At 25° and 35° there was no splitting out of halogen in the case of the β -chlor-ethyl acetate, and none from the β -brom-ester at 25°. At 35° and 45°, however, the β -brom-ethyl acetate was found to decompose slightly in this way, and at 45° a slight decomposition was indicated in the case of the β -chlor-ethyl acetate, which was so small as to be negligible. The necessary correction for the formation of halogen acid was applied to the titrations made at 35° and 45° in the hydrolysis of the β -brom-ethyl acetate, where as much as 4 per cent to 4.5 per cent of the halogen was found to be set free as halogen acid.

From the titrations made as described above the velocity constants recorded in Table I were calculated by using the titration formula for monomolecular reactions:

$$K = \frac{2.3}{t} \left[\log (T_{\infty} - T_0) - \log (T_{\infty} - T_n) \right],$$

where T_0 is the initial titration, T_{∞} the final titration, and T_n an intermediate titration all expressed in cubic centimeters of decinormal sodium hydroxide, and t represents the time interval in minutes between the initial titration T_0 and that represented by T_n .

On referring to Table II it is seen that the substitution of chlorine, of hydroxyl, and of ethoxyl groups in the beta position produces practically the same retardation of the rate of hydrolysis in each case. The substitution of bromine in the beta position produces a retardation of the hydrolysis which is considerably less than that produced by the chlorine substitution. The ethoxyl group produces a slightly greater retardation than the methoxyl group.

The temperature coefficients are found to vary from 2.2 to 2.5 for an increase of ten degrees. The substitution of bromine in the beta position has a lowering effect upon the temperature coefficient. In the case of other esters of this series the coefficients were found to be practically constant, having the values of 2.5 for the range from 25°–35° and 2.3 to 2.4 for the increase from 35°–45°.

Summary.

1. The β -hydroxy-ethyl acetate may be prepared by refluxing equimolecular quantities of ethylene glycol and glacial acetic acid for eight hours over twice the theoretical quantity of anhydrous copper sulphate.

2. By heating equimolecular quantities of ethylene dibromide and freshly fused potassium acetate on a water bath for

TABLE I.
Hydrolysis at 25° in decinormal hydrochloric acid.

Ester	β -hydroxy-ethyl acetate	β -methoxy-ethyl acetate	β -ethoxy-ethyl acetate	β -chlor-ethyl acetate	β -brom-ethyl acetate
Time.....	2830	----	3300	2943	2835
$K \times 10^5$	{ 46.2		46.8	47.4	53.3
	{ 47.4		47.1	46.5	54.2
	{ 47.1		46.6	46.3	54.0
	{ 46.9		46.2	46.0	55.4
	{ 47.3		46.1	46.0	55.8
	{ 47.2		46.5	47.4	56.0
	{ 47.6		45.5	46.1	56.9
Averages	47.1		46.4	46.5	55.1
Averages (duplicate)	47.2		46.6	47.2	56.5

Hydrolysis at 35° in decinormal hydrochloric acid.

Time.....	660	840	870	660	660
$K \times 10^5$	{ (111.8)	122.8	117.8	115.5	
	{ 115.6	121.2	117.3	117.5	(109.3)
	{ 117.8	119.6	117.0	118.4	124.2
	{ 117.6	122.3	118.2	118.2	132.2
	{ 117.9	122.6	117.2	117.4	135.5
	{ 117.2	123.4	117.5	117.6	139.7
	{ 118.6	123.7	118.5	118.6	140.7
Averages	117.4	122.2	117.6	117.6	134.5
Averages (duplicate)	117.2	122.8	117.7	117.6	134.8

Hydrolysis at 45° in decinormal hydrochloric acid.

Time.....	210	212	213	210	210
$K \times 10^5$	{ (252)	(259)	(277)	(252)	
	{ 280	281	279	271	(226)
	{ 278	281	279	272	288
	{ 278	280	278	273	297
	{ 278	283	279	278	298
	{ 279	283	280	277	306
	{ 280	282	280	278	300
Averages	279	282	279	275	298
Averages (duplicate)	279	281	280	275	297

TABLE II—SUMMARY.

Temperature	K $\times 10^5$ 25°	K $\times 10^5$ 35°	K $\times 10^5$ 45°	Temp. Coeff. 25°-35°	Temp. Coeff. 35°-45°
Ethyl acetate	64.7	162.1	379.	2.5	2.3
	64.8	161.9	376.		
β -hydroxy-ethyl acetate	47.1	117.4	279.	2.5	2.4
	47.2	117.2	279.		
β -methoxy-ethyl acetate	--	122.2	282.	--	2.3
	--	122.8	281.		
β -ethoxy-ethyl acetate	46.6	117.6	279.	2.5	2.4
	46.4	117.7	280.		
β -chlor-ethyl acetate	55.1	134.5	298.	2.4	2.2
	56.5	134.8	298.		

eighteen hours, the product obtained is glycol diacetate and not the β -hydroxy-ethyl acetate.

3. β -ethoxy-ethyl alcohol is formed by digesting equimolecular quantities of β -brom-ethyl acetate and sodium ethylate for half an hour in alcoholic solution.

4. The substitution of halogen or an alkoxy group in the alpha position of the alkyl radical of an ester accelerates the decomposition of the ester to such an extent that the reaction velocity is not measurable. In the case of all three esters of this type that were hydrolyzed acetaldehyde formed one of the hydrolysis products.

5. The substitution of hydroxyl, alkoxy, or halogen in the beta position of the alkyl radical produces a considerable retardation on the rate of hydrolysis. In the case of the esters derived from the beta substituted ethyl alcohols it was found that the hydroxyl and ethoxy groups and chlorine produce practically the same degree of retardation.

6. The ethoxy group produces a slightly greater retardation than the methoxy group.

7. The introduction of halogen in the beta position of the alkyl radical produces a retardation of the rate of hydrolysis. In the case of the β -brom-ethyl acetate this retardation is less than in the case of the β -chlor-ethyl acetate.

8. The temperature coefficients in the case of the esters derived from the beta substituted alcohols are found to vary from 2.2 to 2.5 for an increase of ten degrees. The substitution of bromine in the beta position has a lowering effect upon the temperature coefficient.