

ART. LI.—*On the Hydrolysis of Esters of Substituted Aliphatic Acids*; by E. W. DEAN.

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

6. SAPONIFICATION BY SODIUM HYDROXIDE OF HYDROXY AND ALKYL OXY ACETATES AND PROPIONATES.

General Discussion.

HAVING recently determined the velocity constants of several esters for their hydrolysis in decinormal acid, it was decided to continue the study by measurements taken in alkaline solution.

Considerable work has been done in this line in connection with the theory of steric hindrance and some of the esters in the list included in this paper have been examined before. Brief mention is made of the researches which have more or less important bearing upon the experiments here described.

The velocity of saponification of ethyl acetate seems to have been measured first by Warder.* Soon after came a series of very accurate and comprehensive measurements by Reicher.† He determined the relative effects of various bases and also showed that the effect of the alcohol radical in the ester is practically constant. Methyl esters decompose most rapidly and the velocity decreases up the series. The differences, however, are exceedingly slight beyond about the first three members. Reicher's experiments with the esters of different acids pointed toward a decrease in velocity with increasing molecular weight.

The effect of the presence of neutral salts on the velocity of saponification has been studied by Arrhenius‡ and by Armstrong and Watson.§ Measurements have been made by Hjelt|| on esters of polybasic acids and by Goldschmidt¶ on acetacetic ester. The most important work in the present connection is that of Findlay and Turner** and Findlay and Hickmans.†† Here careful determinations have been made of the effect of hydroxyl and alkyl oxy groups on the velocity of reaction. In two cases the esters saponified have been included in the series considered in this paper. The results of this work will be taken up in detail later.

Preparation of Material.

The esters used were in general portions of the same samples hydrolyzed in acid solution, results of which work‡‡ have been

* Ber., xiv, 1361.

† Ann., cccxviii, 251.

‡ Zeitschr. phys. Chem., i, 110.

§ Proc. Royal Soc., Series A, lxxix, 564.

|| Ber., xxix, 110; xxxi, 1844.

¶ Ibid., xxxii, 3396.

** Jour. Chem. Soc., lxxxvii, 747.

†† Ibid., xcv, 1004.

‡‡ This Journal, xxxiv, 293.

fully described. The list included ethyl acetate, ethyl glycolate, three alkyloxy acetates, ethyl propionate, ethyl lactate, and ethyl alpha and beta ethyloxy propionates. The methods of preparation and properties of these esters need no discussion here.

Solutions of hundredth normal barium hydroxide and approximately fortieth normal sodium hydroxide were prepared free from carbonate by the usual methods. Hundredth normal hydrochloric acid was prepared and standardized by silver precipitation.

Procedure.

Measurements were made of reactions at two temperatures, zero degrees and twenty-five degrees. For the former series was used a small thermostat filled with ice and water and vigorously stirred. A temperature constant within a tenth of a degree was easily maintained in this manner. For work at twenty-five degrees the thermostat fully described in a previous paper* was employed.

The actual experiments were carried on by a slight modification of the method recommended by Ostwald.† In the thermostat were placed two flasks, one containing a measured amount of fortieth normal sodium hydroxide solution, the other a solution of the ester of slightly smaller concentration than that of the alkali. At the proper time an amount of the ester solution equal to that taken of the sodium hydroxide was withdrawn by means of a pipette and allowed to flow rapidly into the reaction flask. This was shaken vigorously, replaced in the thermostat and a ten cubic centimeter portion removed and allowed to run into a known quantity (15 cm^3) of hundredth normal hydrochloric acid. The excess of acid was then determined by titration with centinormal barium hydroxide. Rosolic acid was used as an indicator, this having been proven by experience to be better than phenolphthalein under the conditions described.

To obtain good constants by the method thus described requires a moderate amount of skill in manipulation. We are at present unable to compare its advantages with those of the conductivity method of Walker,‡ employed by Findlay and Hickmans.§ We therefore limit ourselves to stating the sources of error and the precautions adopted. In order to be able to check the reaction abruptly at the end of any interval of time, a pipette which discharged the major portion of its contents in four or five seconds was used. By vigorously rotating the flask into which the pipette was emptied the alkali was

* This Journal, xxx, 72.

† Ostwald-Luther, *Physiko-Chemische Messungen*, 3d ed., p. 529.

‡ Proc. Roy. Soc., Series A., lxxviii, 157.

§ Loc. cit.

immediately neutralized by the excess of acid present. In this way a very sharp end-point was obtained, since in acid of such dilution the velocity of decomposition of any ester is negligible. It seems probable that irregularities in constants caused in this way are very slight, especially in view of the fact that uniform procedure was adopted for all measurements. The principal cause of irregularities is the difficulty of titrating accurately with such dilute solutions in the presence of relatively large amounts of salts of the organic acids. On the whole, however, reasonably good constants were obtained even in cases where the reaction proceeded with considerable velocity.

Calculations were made by the use of the titration formula* for reactions of the second order.

$$K = \frac{1}{.4343 \cdot t \cdot T_{\infty}} \cdot \frac{V}{n} \cdot [\log T + \log (T_0 - T_{\infty}) - \log T_0 - \log (T - T_0)]$$

T is the amount of HCl consumed by the excess of NaOH at the time t . T_0 is the initial titration and T_{∞} the titration value of the excess of NaOH at the end of the reaction. All values of T were of course obtained indirectly by subtraction of the quantities of barium hydroxide from the fifteen cubic centimeters of acid employed. V is the volume of the pipette, and N the normality of the hydrochloric acid in terms of which the reaction was measured.

In the tables are given the values of K and of the periods in minutes over which the reactions proceeded with measurable velocity.

TABLE I.

Reaction at 0°.					
Ester.....	Ethyl acetate	Ethyl glycolate	Ethyl methoxyacetate	Ethyl ethoxyacetate	Ethyl propoxyacetate
Time.....	300	35	25	25	25
K	1.24	13.8	36.7	13.8	12.6
	1.21	13.5	39.5	18.6	12.8
	1.20	(9.7)	40.3	16.8	13.8
	1.14	12.3	37.7	15.8	12.9
	1.13	12.6	36.4	14.5	13.0
	1.11	12.4	33.7	15.4	11.4
	1.16	---	30.5	---	12.3
Averages..	1.17	12.9	36.4	15.9	12.7
Averages..	1.19	12.8	37.1	15.2	12.9
(duplicate)					

* Findlay, Practical Physical Chemistry, p. 243. Ostwald-Luther, loc. cit.

TABLE I (continued).

Reaction at 25°.					
Ester.....	Ethyl acetate	Ethyl glycollate	Ethyl methoxy acetate	Ethyl ethoxy acetate	Ethyl propoxy acetate
Time.....	60	10	5	15	12
K	{ 6·60	(56·4)	156·	66·4	52·8
	{ 6·60	65·7	146·	62·4	(59·8)
	{ 6·85	67·6	119·	62·4	51·7
	{ 6·63	61·7	117·	62·3	52·8
	{ 5·89	68·6	104·	70·2	51·3
	{ 6·78	63·0	---	65·3	---
Averages..	6·56	65·3	128·	64·8	52·1
Averages.. (duplicate)	6·54	65·3	118·	61·8	49·1

TABLE II.

Reaction at 0°.					
Ester.....	Ethyl propionate	Ethyl lactate	Ethyl glycerate	Ethyl α ethoxy propionate	Ethyl β ethoxy propionate
Time.....	275	25	25	180	185
K	{ 1·24	14·4	9·40	2·57	1·15
	{ 1·15	15·3	9·80	2·09	1·15
	{ 1·12	14·5	9·20	2·09	1·13
	{ 1·20	13·8	8·70	1·98	0·98
	{ 1·11	14·4	8·88	1·89	1·00
	{ 1·05	14·6	8·15	1·81	1·02
Averages..	1·14	14·6	9·02	2·07	1·07
Averages.. (duplicate)	1·18	14·3	11·2	1·92	1·10

Reaction at 25°.					
Time.....	90	10	10	110	80
K	{ 5·82	63·9	52·6	9·52	5·63
	{ 5·88	64·1	53·2	9·12	5·28
	{ 6·17	63·8	57·2	8·76	5·20
	{ 6·31	68·3	55·3	9·06	4·93
	{ 6·13	62·5	57·8	10·0	5·14
	{ 5·73	59·7	60·1	---	5·02
	{ 5·88	---	64·6	---	4·46
Averages..	5·94	63·7	57·3	9·29	5·02
Averages.. (duplicate)	6·16	64·6	59·4	9·33	4·87

TABLE III.—Summary.

A				B		
Ester.....	K(0°)	K(25°)	k(aff)*	Ester.....	K(25°)	k(aff)*
Ethyl acetate	1.17	6.56	.0018	Ethyl acetate	6.5	.0018
Ethyl glycolate	12.9	65.3	.0152	Ethyl glycolate	75.	.0152
Ethyl methyl-oxy acetate	36.4	128.	.0335			
Ethyl ethyl-oxy acetate	15.9	64.8	.0234	Ethyl propionate	5.3	.00134
Ethyl propyl-oxy acetate	12.7	52.1	----	Ethyl lactate	63.5	.0138
Ethyl propionate	1.14	5.94	.00134	Ethyl phenylacetate	12.4	.0056
Ethyl lactate	14.6	63.7	.0138	Ethyl mandelate	66.	.0417
Ethyl glycerate	9.02	57.3	.0228	Ethyl methyl-oxy phenylacetate	23.	.074
				Ethyl ethyl-oxy phenylacetate	15.7	.053
Ethyl alpha-ethyloxy propionate	2.07	9.29	----	Ethyl propyl-oxy phenylacetate	13.3	.049
Ethyl beta-ethyloxy propionate	1.07	5.02	----			

Discussion of Results.

In the first part of the summary table are given the averages of the series printed in full in Tables I and II. In addition are stated the dissociation constants of some of the acids as determined by Ostwald. The second part of the table contains results taken from the paper of Findlay and Hickmans,† which seem to be of interest in relation to our work. The figures in two cases do not agree, and this discrepancy is deserving of slight discussion. Our constants for ethyl glycollate saponified at twenty-five degrees are much lower than those of Findlay. After a study of the possibilities of error in our method we are of the opinion that Findlay's results, obtained by the conductivity method, may be the more accurate. We have not, however, been able to duplicate his results. In the other case, that of ethyl propionate, we are convinced that Findlay's figure is decidedly too low. Calculations from the results of Reicher,‡ obtained at a lower temperature, indicate a value of 5.7+. Our value of 5.9 is nearer than that of Findlay, which is 5.3. In addition we would say that it is probable that the figures for

* Ostwald, *Zeitschr. phys. Chem.*, iii, 176. Findlay and Turner, *Jour. Chem. Soc.*, xcv.

† Loc. cit.

‡ Loc. cit.

some of the other esters in our list are probably too low for the work at twenty-five degrees. The ratios obtained from the constants for zero degrees have been considered of more weight in the study of the results.

After a fairly close examination of the above figures we have been unsuccessful in an attempt to obtain conclusions of very general value. The one thing most apparent is that the velocity of saponification of the ester is closely connected with the strength of the acid from which it is derived. This is in accord with the theory set forth by both Hjelt* and Sudborough,† that the velocity of saponification is controlled by two factors, the strength of the acid and steric influences in the molecule. At present we are unable to obtain any mathematical expression which will be of value in predicting the magnitude or direction of these steric influences.

Two or three points brought out by the tables deserve mention. The effect of alkyloxy groups is very varied. Extreme cases are those of the esters of methyloxy acetic and beta ethyloxy propionic acids, which have respectively the greatest and least velocities of all the series. The effect of the hydroxyl group is nearly the same in the cases of glycollate and lactate, but is decidedly less in the case of ethyl mandelate. In ethyl glycerate steric influences prevent any logical comparison. Finally it is to be noted that the ratios of saponification of these esters are entirely different from those of their velocity of hydrolysis in acid solution.

Summary.

1. The presence of a hydroxyl group in aliphatic esters seems to produce an acceleration in the velocity of saponification, although this effect is variable in its magnitude.

2. (a) Alkyloxy groups may cause an effect varying from a tremendous acceleration to a slight retardation in different cases.

(b) The velocity of saponification of alkyloxy esters of similar constitution decreases with the size of the substituted group.

3. Beta substituted esters seem to decompose less rapidly than isomeric alpha products, a single point of resemblance to effects produced in acid hydrolysis.

4. The velocity of saponification is very largely controlled by the strength of the acid from which the ester is derived.

It is our intention to continue this study on the velocities of several other esters and obtain if possible data which will enable us to draw more general conclusions on the subject.

* Loc. cit.

† Proc. Chem. Soc., xiii, 241.