The Acid Catalyzed Hydrolysis of Ethyl Esters of Aliphatic Acids

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In two recent articles[1,2] the effect of the structure of an aliphatic acid upon the velocity of its acid-catalyzed esterification in methanol and upon the rate of saponification of its ethyl ester in 85% ethanol has been discussed. The purpose of the present paper is to report a similar study of the effect of structure on the velocity of acid-catalyzed hydrolysis of ethyl esters of various aliphatic acids. Measurements of equilibrium constants for the hydrolysis of esters show that substitution has little effect on the position of equilibrium. This can be true only if such substituents have essentially the same effect on the rate of acid hydrolysis of an ester as on the rate of esterification of the corresponding acid.[3] In addition, available data indicate that substitution in the acidic group of an ester causes similar changes in the rates of acid and alkaline hydrolysis.[4]

Several publications dealing with the subject of acid hydrolysis of aliphatic esters appear in recent literature. In particular, there is the work of Salmi[5,6] in which rate measurements were made only at 25°, and that of Davies and Evans,[7] in which the rate constants were determined in 70% acetone solution at three temperatures.

Those results of Salmi which deal with esters of normal acids indicate a rather complete parallelism with esterification and saponification in that the rate constants for butyric and higher acids or esters are, within experimental error, the same. He also reports results for simple branched chain esters which are quite similar to those for the other processes.

Davies and Evans, on the other hand, give results which differ from esterification and saponification studies in that the rate constants continue to fall off steadily when the chain length of the normal acid component is increased beyond that of butyric acid. They find, however, that activation energies are constant throughout the normal series. This latter result is also found for other processes.[1,2] Their findings, which involve simple branched chains, also differ from esterification and saponification in that their activation energy for ethyl isobutyrate is about 1000 calories per mole less than that for esters of normal acids. For esterification[1,8] and saponification,[2,9] this is not found.

It seemed desirable to check these discrepancies, and also to extend these studies to include other aliphatic esters which have been used in esterification and saponification experiments.

Experimental

The best grade of ethyl esters of n-butyric, isobutyric, n-caproic, and pelargonic acids was purchased from the Eastman Kodak Company. About 1% of the corresponding acid was mixed with each ester (with the exception of ethyl pelargonate) and a drop of sulfuric acid was added. The purpose of this was to esterify any free alcohol which might be present and thus prevent the formation of azeotropic mixtures. The esters were then fractionated. A five-foot (1.5-meter) spiral column was used for the distillation of the n-butyrate and the n-caproate, a five-foot Vigreux column for the isobutyrate, and the ethyl pelargonate was distilled under diminished pressure in a small two-foot (0.6-meter) Vigreux column.

The esters were analyzed by allowing weighed samples to stand several hours in a 70° bath with excess potassium hydroxide. The unused alkali was then titrated with standard acid. Each of the esters analyzed between 99.4 and 100.3%; the limits of the precision of this analysis method are considered to be about ±0.5%. No free acid was present in any of the esters used.

Purified samples of ethyl cyclohexanecarboxylate, ethyl isocaproate, and ethyl β-methylvalerate were furnished by H. S. Levenson.[2,10]

One-ml. pipets were calibrated for each ester, so that the exact weight (±0.2%) of ester delivered from the pipet was known.

The purified acetone for preparing the reaction medium was obtained by fractionating U. S. P. acetone from alkaline permanganate in a five-foot, spiral-packed column. The fraction retained distilled at constant head temperature.

Davies and Evans ran their hydrolysis experiments in 70% acetone by volume, and with 0.05 N solutions of ester and catalyst (HCl). The conditions used here were similar with the exception that the ester and catalyst were made 0.1 N. Preliminary work established the fact that this change caused a slight lowering (about 5%) of the rate constants at each temperature.

(1) Smith, THIS JOURNAL, **62**, 1136 (1940).

(2) Levenson and Smith, ibid., **62**, 1556 (1940).

(3) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 213.

(4) Cf. Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 451.

(5) Salmi, Ann. Acad. Sci. Fennicae, **A48**, 17 (1937).

(6) Salmi, Ber., **72B**, 1767 (1939).

(7) Davies and Evans, J. Chem. Soc., 339 (1940).

(8) Smith, THIS JOURNAL, **61**, 1176 (1939).

(9) Smith and McReynolds, ibid., **61**, 1963 (1939).

(10) Smith and Levenson, ibid., **62**, 2733 (1940).

Owing to the slow rate of the reaction and the volatility of the solvent, the reaction vessels consisted of Pyrex flasks the openings of which were fitted with glass plugs. A rubber sleeve around the opening and the plug prevented loss of solvent by evaporation.

Aqueous solutions of acetone and 0.6 N hydrochloric acid were prepared so that when one ml. of ester was added, the concentration of ester and hydrochloric acid each would be 0.1 N in 70% (by volume) acetone. In making up such solutions, it was necessary to consider the net decrease in volume observed when acetone and water are mixed. Expansion measurements were used in correcting for changes of concentration due to thermal expansion of the solvent.

The mixtures so prepared were placed in electrically controlled water thermostats which gave temperatures constant to $\pm 0.01°$, at 20, 30, 40 and 50°. After temperature equilibrium had been established, the ester was added, and the contents of the flask thoroughly mixed. The reaction was followed by pipetting 10-ml. portions from the flask at suitable intervals, and titrating the acid present with 0.04 N standard carbonate-free sodium hydroxide using phenolphthalein indicator.

Experimental Calculations and Results

The rate constants were calculated using the expression

$$k = \frac{2.303 \log a/(a - x)}{(\text{catalyst}) \, t}$$

where a is the initial ester concentration, x is the concentration of organic acid formed after time t, and the (catalyst) is the concentration of added hydrochloric acid. Table I gives the results of a typical run. Because of the reverse esterification

TABLE I

ACID CATALYZED HYDROLYSIS OF ETHYL ISOBUTYRATE IN 70% ACETONE AT 30°

a = (ester) = (HCl) = 0.100

t, minutes	$(a - x)$	$10^5 k$, liters mole^{-1} sec.$^{-1}$
6	0.09965	....
1595	.08190	2.05
2465	.07395	2.04
3116	.06737	2.11
3953	.06176	2.03
5389	.05018	2.13
6734	.04179	2.16
	Average, 18–50%	2.07

TABLE II

REACTION RATE CONSTANTS FOR ACID HYDROLYSIS OF ETHYL ESTERS OF ALIPHATIC ACIDS IN 70% ACETONE

a = (ester) = (HCl) = 0.1 M

Ethyl ester	$t = 20°$	$t = 30°$	$t = 40°$	$t = 50°$
	$k \times 10^5$ (liters mole^{-1} sec.$^{-1}$)			
n-Butyrate	1.10	2.88	6.90	15.8
	1.08	3.11	6.93	16.1
	1.17	2.98		15.7
	1.14			
	1.21			
Av.	1.14	2.99	6.92	15.9
n-Caproate	1.09	2.80	6.70	14.8
	1.12	2.82	6.75	15.4
Av.	1.10	2.81	6.72	15.1
n-Pelargonate	0.865	2.20	5.16	11.8
	.870	2.19	5.21	11.8
Av.	.868	2.20	5.19	11.8
Isobutyrate	.865	2.05	5.07	11.6
	.868	2.07	5.04	11.7
	.863	2.09	4.98	
		2.07	5.04	
		2.05		
		2.07		
Av.	.865	2.07	5.03	11.7
β-Methyl-valerate	.248	0.660	1.52	3.52
	.251	.621	1.51	3.58
		.656		
Av.	.250	.646	1.52	3.55
Isocaproate	1.05	2.87	6.18	14.5
	1.03	2.59	6.14	
	1.06	2.59		
	1.00			
Av.	1.04	2.68	6.16	14.5
Cyclohexane-carboxylate	0.466	1.14	2.62	6.23
	.471	1.16	2.62	6.16
	.483			6.18
				6.22
Av.	.473	1.15	2.62	6.20

reaction and also the possibility of loss of solvent each time a sample was withdrawn, the individual k values were averaged over the range of approximately 20–50% reaction. The number of values averaged was usually four or five, and the $\pm$ errors of the order of one or two per cent. The average k for each run is listed in Table II.

TABLE III

k_{25} AND E FOR ACID HYDROLYSIS OF ETHYL ESTERS OF ALIPHATIC ACIDS

Ethyl ester	Present research		Davies and Evans[7]	
	$10^5 k$	E	$10^5 k$	E
Acetate			4.55	16,200
Propionate			3.77	16,300
n-Butyrate	1.86	16,500	2.00	16,400
n-Valerate			1.82	16,500
n-Caproate	1.77	16,400	1.80	16,200
n-Heptoate			1.67	16,200
n-Octoate			1.58	16,300
n-Pelargonate	1.40	16,400		
Isobutyrate	1.35	16,400	1.49	15,200
Isovalerate			0.583	16,600
Isocaproate	1.68	16,400		
β-Methylvalerate	0.405	16,600		
Trimethylacetate			0.131	a
Diethylacetate			0.120	19,000
Cyclohexane-carboxylate	0.740	16,100		

a The data of Davies and Evans do not give a straight line when log k is plotted against $1/T$ for this ester. However, the points indicate a minimum value of at least 19,000 cal./mole.

The plots of log k against $1/T$ for the hydrolysis of these esters are given in Figs. 1 and 2. The ac-
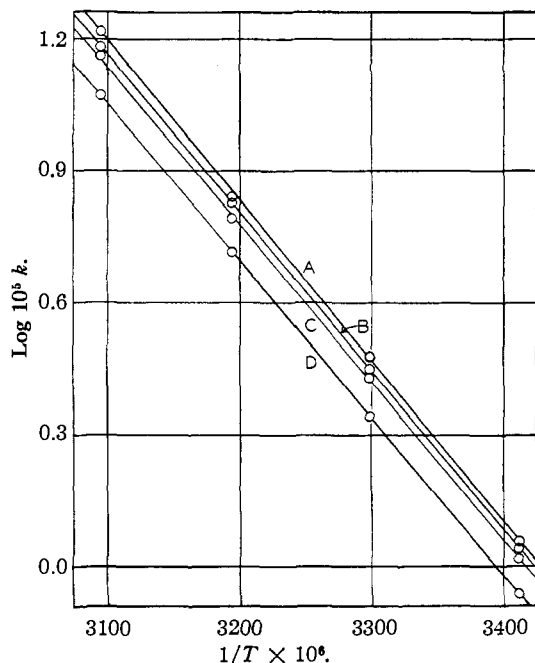

Fig. 1.—Temperature coefficients for acid hydrolysis of aliphatic esters: A, ethyl n-butyrate; B, ethyl n-caproate; C, ethyl isocaproate; D, ethyl pelargonate.
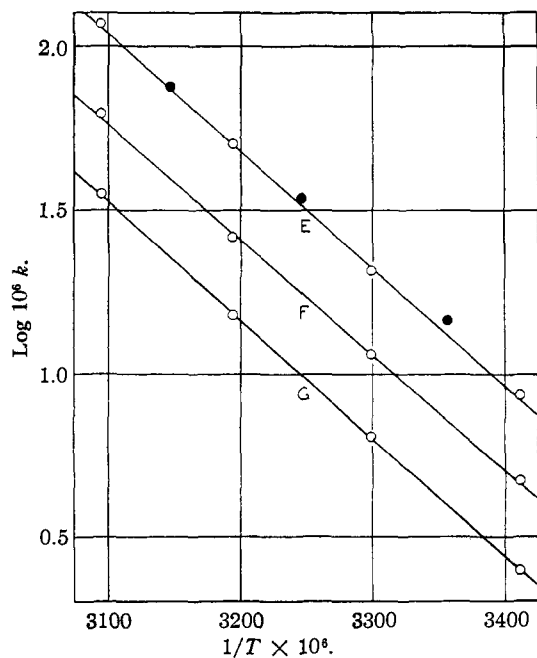

Fig. 2.—Temperature coefficients for acid hydrolysis of aliphatic esters: E, ethyl isobutyrate; F, ethyl cyclohexanecarboxylate; G, ethyl β-methylvalerate; O, points from data of Smith and Steele; ● points from data of Davies and Evans.[8]

tivation energies were calculated from the slopes of these lines, and were checked by the method of least squares. They are reported to the nearest 100 calories. These and k_{25} interpolated from Table II together with similar values calculated from the data of Davies and Evans on hydrolysis of various aliphatic esters are recorded in Table III.

Discussion

The results of studies of acid-catalyzed hydrolysis of ethyl esters of aliphatic acids in 70% acetone as given in Table III correspond to those of alkaline hydrolysis in 85% ethanol and of acid catalyzed esterification in absolute methanol. The only apparent difference lies in the fact that the rate of acid hydrolysis of the esters does decrease slightly with increasing chain length beyond ethyl butyrate. Since this result was not found by Salmi,[5,6] it is probably caused by some specific effect of the character of the solvent employed. Experiments on saponification of these esters in the same medium[7] also indicate this solvent effect. The decrease is, however, minor when compared with the changes in k when one proceeds from acetate to propionate to butyrate.

Davies and Evans' low activation energy for ethyl isobutyrate is not confirmed, but rather E seems to be the same as for esters of normal acids. The explanation of the low value of the activation energy for ethyl isobutyrate hydrolysis in the light of the Baker–Nathan effect[11,12] is thus rendered unnecessary.

The result of increased methyl substitution in the α position of acetic acid (or of its ethyl ester) is the same in the three processes. The decrease in k becomes greater with increased substitution, the activation energy being constant for acetate, propionate, and isobutyrate, but showing a marked rise with the substitution of the third CH_3 group to make trimethylacetate.

The rate constants for acid hydrolysis of the isobutyrate, isovalerate, β-methylvalerate, and isocaproate again indicate that substitution must take place in the α or β position in order to cause appreciable diminution in k. The isocaproate is hydrolyzed a very little more slowly than the un-

(11) Cf. Evans, Gordon and Watson, J. Chem. Soc., 1439 (1938).

(12) The Baker–Nathan effect postulates that the electron pair or pairs linking carbon to hydrogen in one of the groups —CH_3, —CH_2R, or —CHR_2 come under the influence of the adjacent carbon atom. In a system involving a double bond, a type of conjugation may take place, resulting in the inversion of the normal order of the effect of substitution, the order becomes namely: $CH_3 > CH_3CH_2 > (CH_3)_2$-$CH > (CH_3)_3C$. See J. Chem. Soc., 1844 (1935).

substituted n-valeric ester, but this difference is negligible when compared to those between iso-butyrate and propionate, or isovalerate and butyrate. The slight difference observed is probably due to the same factors which cause a slight decrease in k for higher members of the normal series.

Simultaneous lengthening of two normal chains also appears to be similar for the processes of esterification, saponification and acid hydrolysis. Thus the change from acetate to isobutyrate has relatively little effect when compared to that between isobutyrate and diethylacetate. However, when the ends of the diethylacetate chains are linked together with a methylene group to form ethyl cyclohexanecarboxylate, the resulting ester behaves much more like the isobutyrate than like the diethylacetate, both in k and E. This is shown in Table IV for the three processes, and can be explained along lines previously suggested.[8]

TABLE IV

Acid or ester	Esterification		Saponification		Acid Hydrolysis	
	10^3k_{25}	E	$10k_{25}$	E	10^5k_{25}	E
Isobutyrate	19.7	9,800	8.01	15,000	1.35	16,400
Cyclohexane-carboxylate	11.9	10,000	3.60	15,600	0.742	16,100
Diethylacetate	0.504	12,400	0.154	17,200	0.120	19,100

Thus, the effect of the character of an alkyl group on the rate of acid-catalyzed hydrolysis of ethyl esters of aliphatic acids is essentially the same as its effect on saponification of the same ester or of the acid-catalyzed esterification of the corresponding organic acid.

Note on the Saponification Reaction

It has been demonstrated previously[13] that the activation energy for saponification of ethyl esters of normal acids is constant, within experimental error, regardless of the alkyl chain length of the acid. This conclusion has been questioned in two subsequent papers. Shrivastava[14] studied saponification of certain aliphatic esters in dilute solution and, as a result of his work, states, "In the case of normal esters also the value of PZ changes from ester to ester, but at the same time a progressive, though slight, increase in the value of E with increasing chain length is at once evident from the results tabulated above. It may be argued that these variations may be only apparent and may easily be accounted for by slight experimental errors as in fact almost all the values of E lie within the range 10,400 ± 400 cal. But it is somewhat remarkable that the increase is almost regular."

The above statements are in error due to two causes. In the first place, the author considers ethyl esters only, ignor-

(13) Smith and Levenson, THIS JOURNAL, **61**, 1172 (1939).
(14) Shrivastava, J. Indian Chem. Soc., **17**, 370 (1940).

ing his corresponding series of methyl esters. In the second place, his calculations of E are inaccurate. In Table V are given the mathematically (least squares) calculated activation energies for these series as obtained from the data of Shrivastava. An examination of these figures fails to show progressive changes in E, and offers no evidence that variations in E are due to other than experimental errors.

TABLE V
ACTIVATION ENERGIES RECALCULATED FROM THE DATA OF SHRIVASTAVA[14]

	E, methyl ester	E, ethyl ester
Acetate	9,800	10,600
Propionate	11,400	10,500
Butyrate	10,500	11,000

The second paper in which the constancy of the activation energy for the normal series is questioned is that of Davies and Evans[7] in which they report results of investigations of the saponification of aliphatic esters in 70% aqueous acetone. The activation energies as reported do show progressive increases as the acid chain is lengthened. However, examination of their data indicates that their reactions are extremely fast. For instance, their fastest run with acetate gives 50% reaction in about two and one-half minutes, for propionate in about five minutes, and longer times for higher esters. Any systematic error such as timing of the start of the reaction, or cooling of the reaction mixture as it is drawn into a pipet before analysis, would readily cause the apparent variation in E recorded. As pointed out by Davies and Evans, a comparison of their results with those of Newling and Hinshelwood[15] shows that E for ethyl isobutyrate is essentially the same in 70 or 56% acetone, while the E for ethyl acetate in 70% acetone is almost 2000 cal./mole lower than the corresponding value for methyl acetate in 56% acetone. Since substitution of methyl for ethyl makes little difference in E (cf. Table V), it seems obvious that one of these figures is in error. Until the results of Davies and Evans have been checked under experimental conditions leading to longer time intervals, they are open to considerable question.

Summary

The kinetics of acid catalyzed hydrolysis in 70% acetone has been studied for ethyl butyrate, ethyl caproate, ethyl pelargonate, ethyl isobutyrate, ethyl β-methylvalerate, ethyl isocaproate, and ethyl cyclohexanecarboxylate.

From a combination of the results obtained with those previously published by Davies and Evans, it appears that the effect of the character of an alkyl group on the rate of acid and base-catalyzed hydrolysis of aliphatic acid esters and on the rate of acid-catalyzed esterification of the corresponding acids is similar.

(15) Newling and Hinshelwood, J. Chem. Soc., 1357 (1936).