

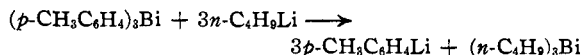
separated. Removal of the ether left a solid which when recrystallized from hot ethanol melted at 121–122°; yield 78%.

Anal. Calcd. for $C_{24}H_{27}O_3Bi$: Bi, 36.53. Found: Bi, 36.49 and 36.77.

A mixture of 0.01 mole of tri-*o*-ethoxyphenylbismuth and 0.03 mole of *n*-butyllithium in 165 cc. of ether was refluxed for eleven hours. Carbonation gave a 64% yield of *o*-ethoxybenzoic acid, characterized by a mixed melting point determination of its menthyl ester. From this reaction as well as from the interconversion reaction with tri-*p*-ethoxyphenylbismuth, there were also formed tri-*n*-butylbismuth and *n*-valeric acid.

Summary

Triarylbiomuth compounds and organoalkali compounds undergo the following typical interconversion reaction



There is no evidence of nuclear metalation.

Tri-*n*-butylbismuth is oxidized with explosive violence by oxygen, and an aldehyde appears to be one of the preliminary products of oxidation.

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[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Kinetics of the Saponification of the Ethyl Esters of Normal Aliphatic Acids

BY HILTON A. SMITH AND H. S. LEVENSON

Recently two papers have been published which deal with the effect of the length of the carbon chain in the normal aliphatic series on the kinetics of some chemical process. The first¹ deals with the base catalyzed hydrolysis or saponification of ethyl esters of a number of aliphatic acids, while the second² reports the study of the acid-catalyzed esterification of normal aliphatic acids with methyl alcohol. In both cases the values of the bimolecular rate constants decreased with increasing length of the carbon chain until butyric acid (or ethyl butyrate) was reached. Further lengthening of the chain had no effect on the rate constants.

While the agreement of these two papers as to the actual change in the values of k is excellent, the assignments of the variation of the value of k to the activation energy or to the steric factor in the equation $k = sZe^{-E/RT}$ are at variance with each other. Evans and co-workers state that the variation in k is due entirely to variation in the activation energy, while in the case of the esterification reactions the activation energy is found to be constant. This disagreement does not seem reasonable.

A comparison of the two studies yields the following facts. In the case of the esterification studies, the values of k were determined at four temperatures. The values were found to be in good agreement with those obtained by Williamson and Hinshelwood in the case of acetic acid³

(1) Evans, Gordon and Watson, *J. Chem. Soc.*, 1439 (1938).

(2) Smith, *THIS JOURNAL*, **61**, 254 (1939).

(3) Williamson and Hinshelwood, *Trans. Faraday Soc.*, **30**, 1145 (1934).

and by Goldschmidt in the cases of acetic, propionic, butyric and valeric acids.⁴

Since it is easily possible to make an error of a few per cent. in activation energies as determined by the graphical method, the calculation of the activation energies of the esterification reactions has been checked by the method of least squares. The values obtained in this manner are: formic, 9560; acetic, 9985; propionic, 9834; and higher acids, 9750. These values are all within a range of some 200 cal. with the exception of that for formic acid. This value is low solely for the reason that the k at 40° is low as compared to the three other values. The reaction is so fast at this temperature (half completion in two minutes) that the value may well be a little low. The value of E obtained from the three lower values of k is 9790 cal., which is in excellent agreement with the activation energies of the higher acids. It seems quite improbable that the values of E are in sufficient error to allow the variation of k to be attributed to any variation in E .

In the case of the saponification study, the values of k were determined at three temperatures only. The authors state that the plot of $\log k$ against $1/T$ gives a good straight line in each case. Their data were replotted, and the results showed their statement to be inexact for the early members of the series. There is a considerable variation between the slope of the line connecting the values of $\log k$ between 20 and 35° and that of the line connecting the values of $\log k$ between 35 and

(4) Goldschmidt and Thuesen, *Z. physik. Chem.*, **81**, 30 (1912).

50°. In the case of ethyl propionate, for instance, the mathematically calculated slope of the line connecting the first two values of k results in an activation energy of 15,100 cal. while the slope of the line connecting the 35–50° values is 14,340 cal. This is a variation of 760 cal., which is rather large when one realizes that the authors are attributing significance to variations in E which amount to only a few hundred calories. As a matter of fact, the substitution of the activation energy obtained by averaging the two given above (14,700) for that given by the authors (14,500) brings the activation energies for the saponification of ethyl esters of all but one of the normal acids studied within the range of 14,700 to 15,000 cal. These are certainly constant within experimental error. In the case of ethyl acetate, however, E calculated in the manner indicated above is only 14,030 cal. (the reported figure was 14,200). The two values from which this is computed differ by 500 cal.

An examination of the experimental methods of Evans, Gordon, and Watson indicated that their rate constants might be subject to certain experimental errors, these errors being especially pronounced in the case of ethyl acetate. The authors' claim as to the purity of their compounds rests in the statement that the esters were purchased and purified by repeated fractional distillation. The boiling points were given, in general, to the nearest whole degree. While the distillation may have been carried out in a good fractionating column, no statement is made to that effect. If a simple distilling flask were employed, such a treatment could not be depended on for purification purposes. This is especially true in the case of ethyl acetate (b. p. 77.1°) since this substance has an azeotrope with ethyl alcohol which boils at 71.8°, and another with ethanol and water which boils at 70.3°. ⁵

Their velocity determinations were carried out in the same manner as that used in connection with the study of the alkaline hydrolysis of certain benzoic esters. ⁶ This involves the determination of the amount of ester used in each run by actually weighing the ester in a stoppered 100-ml. flask, and subsequently making up to 75 ml. with alcohol. While this method may be used for solids, or for high boiling liquids, it is not satisfactory for a compound which boils as low as does ethyl acetate.

(5) "I. C. T.," Vol. 111, pp. 320 and 323.

(6) Evans, Gordon and Watson, *J. Chem. Soc.*, 1430 (1937).

This may be seen from the following calculation. The weight of ethyl acetate necessary for the 0.05 M solutions used by the authors is about 0.44 g. If the weighings were made at 25°, the vapor pressure of the ethyl acetate would be about 90 millimeters. This means that if the air in the 100-ml. flask used were saturated with the ester by vaporization from the weighed sample, approximately 0.043 g. or 10% of ester would be vaporized. When the alcohol was poured into the flask, there can be little question but that a fair percentage of this vaporized ester was forced out of the flask, thus causing some difference between the amount of ester weighed out, and the amount of ester which was actually present at the beginning of a run. The error from this source would be considerably lower in the case of ethyl propionate (vapor pressure at 25° is about 35 mm.) and would be essentially negligible for still higher boiling esters.

Since the results of Evans, Gordon, and Watson were subject to the possible errors just outlined, it seemed wise to check the results which they obtained with the low-boiling esters.

Experimental

The best grade of the ethyl esters of acetic, propionic, and butyric acids was purchased from the Eastman Kodak Company. Approximately 3% of the corresponding acid was mixed with each ester, and a drop of sulfuric acid added. This was done to esterify any free alcohol which might be present, and hence prevent the formation of azeotropic mixtures. The esters were then fractionated in a five-foot (1.5-meter) spiral column, the fractions which were saved distilling at a constant head temperature.

The esters were analyzed by allowing weighed samples to stand for one hour in a 70° bath with twice the necessary amount of caustic to cause complete saponification. The unbound alkali was then titrated with standard acid. This method was considered to indicate the purity of the esters with a precision of about 0.5%. All of the esters gave analyses between 99.5 and 100.5%. No free acid was present in any of the esters.

The velocity determinations were carried out in 85% ethyl alcohol. This was made by treating 95% ethanol with silver oxide, and subsequently fractionating the alcohol. The alcohol thus obtained was diluted with distilled water to 85% by weight. The reagent was made up in a large batch in order to give a reproducible medium.

One-ml. pipets were calibrated for each ester, so that the exact amount of ester delivered from the pipet at 20° was known. This value was found to be reproducible to $\pm 0.15\%$. Mixtures of 85% ethanol and of 0.2 N sodium hydroxide in 85% ethanol were made up in glass-stoppered bottles so that when the ester was added, the concentration of ester and of sodium hydroxide would be 0.05 M in each case. The mixtures were allowed to come to temperature equilibrium in electrically controlled water

thermostats, the ester added and the contents of the bottle thoroughly mixed. Zero time was taken at half delivery of the ester. The reaction was followed in the manner described by Evans and co-workers.⁶

Experimental Calculations

The results of a typical run are given in Table I, and the values of k for each ester in Table II. These were calculated using the bimolecular reaction rate equation

$$k = \frac{1}{t} \frac{x}{(a-x)a}$$

where a = initial concentration of each reactant

TABLE I
SAPONIFICATION OF ETHYL ACETATE AT 30°
 $a = (\text{Ester}) = (\text{NaOH}) = 0.05$

t , min.	x	$10^3 k$
4	0.00591	11.2
9	.01142	11.0
15	.01630	10.7
24	.02207	11.0
37	.02717	10.7
53	.03147	10.7
83	.03644	10.8
143	.04105	10.7
322	.04615	12.4

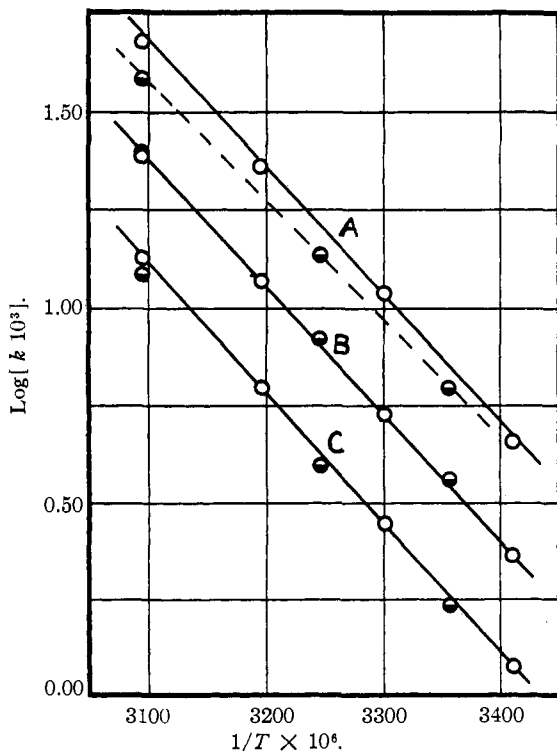


Fig. 1.—Temperature coefficients of saponification reactions: A, ethyl acetate; B, ethyl propionate; C, ethyl butyrate; ○, points from data of Smith and Levenson; ●, points from data of Evans, Gordon and Watson.¹

and x = concentration of each reactant at the time t . The units of k are liters mole⁻¹ sec.⁻¹.

TABLE II

REACTION RATE CONSTANTS FOR THE SAPONIFICATION OF ETHYL ACETATE, ETHYL PROPIONATE, AND ETHYL BUTYRATE

In all cases, (Ester) = (NaOH) = 0.05

Ethyl ester	$k \times 10^3$, liters mole ⁻¹ sec. ⁻¹				
	$t = 20^\circ$	$t = 30^\circ$	$t = 40^\circ$	$t = 50^\circ$	
Acetate	4.56	11.0	22.9	47.6	
	4.51	10.8	23.0	47.6	
				47.7*	
				48.7*	
	Av.	4.53	10.9	22.9	47.9
Propionate	2.32	5.28	11.9	23.9	
	2.33	5.32	11.5	24.4	
	Av.	2.32	5.30	11.7	24.2
Butyrate	1.18	2.79	6.31	13.4	
	1.18	2.79	6.23	13.2	
	Av.	1.18	2.79	6.27	13.3

Because small experimental errors may cause large errors in k during the first and last 20% of each run, such values were not averaged. The average error of each k reported is of the order of 1% and is, in no case, greater than 2%.

In order to make sure that none of the esters was lost by vaporization during delivery from the pipet, two runs were made with ethyl acetate at 50° in which the acetate was added in a slightly different manner. Here the ester was put into the reaction bottle in a sealed bulb. The volumes of 85% alcohol and alcoholic sodium hydroxide necessary to make the concentration of ester and sodium hydroxide each equal to 0.05 molal were added, and the bottle and contents allowed to come to equilibrium in the thermostat. At a given instant, the ampoule was broken under the surface of the liquid, the contents of the bottle thoroughly mixed by shaking, and the reaction followed in the usual manner. The runs made in this way are indicated by an asterisk in Table II.

The plot of $\log k$ against $1/T$ is shown in Fig. 1, in which the values of $\log k$ obtained by Evans, Gordon, and Watson as well as those obtained in the present research are shown.

Discussion

The points in Fig. 1 resulting from the present research fall on a good straight line, and agree quite well with those found by Evans and co-workers for ethyl propionate. The agreement in the case of ethyl butyrate is not too bad, the difference in the 50° values being about 8%. It

is interesting to note in this connection that our value (13.3) is almost identical with the average found by Evans and co-workers for esters of higher normal acids (13.4).

In the case of ethyl acetate, however, the agreement is very poor, the k 's for 50° differing by almost 25%. Not only are our figures greater, but the resulting activation energy is also greater. This is shown in Fig. 1 where the dotted line connects the k values of Evans, Watson, and Gordon. While it is impossible to state the exact reason for this disagreement, we feel that losses by vaporization of the ester are probably to a large extent responsible for the low values of Evans and co-workers.

Table III gives the activation energies for saponification of ethyl esters of normal aliphatic acids. The values for the acetate, propionate, and butyrate are the result of the present research. Those for the higher esters are from the work of Evans, Gordon, and Watson. In all cases the error from the average figure is some 200 cal. or less. These differences easily may be accounted for by experimental error.

TABLE III
ACTIVATION ENERGIES OF SAPONIFICATION OF ETHYL
ESTERS OF NORMAL ALIPHATIC ACIDS

Ethyl ester	Activation energy
Acetate	14,700
Propionate	14,700
Butyrate	15,100
Valerate	14,700
Hexoate	14,800
Heptoate	15,000
Octoate	15,000
Av.	14,900

This being the case, the statements of the previous workers which attribute the changes in velocity of saponification of esters which are not branched at the α carbon atom almost entirely to changes in " E " and indicate that " E " increases

gradually as the normal series is ascended and tends to reach a constant maximum, must be revised. Our conclusions are that " E " is constant within the precision of the measurements for this series of esters, and that changes in the velocity must be attributed to a large extent to changes in " s " in the equation $k = sZe^{-E/RT}$.

Dippy,⁷ in his paper on the dissociation constants of monocarboxylic acids, makes a statement to the effect that an increasing inductive effect with increase in chain length of a normal series necessitates an increase in activation energy of reactions similar to the one studied here. If this is true, there seems to be little point in discussing inductive effects, with the exception of stating that there seems to be no difference in the inductive effects of the normal alkyl groups.

The variations in the value of the reaction velocity constants are much the same as the variations found in the case of the catalyzed esterification of aliphatic acids with methyl alcohol, and evidently must be explained on the same basis.

Summary

The kinetics of the saponification of the ethyl esters of acetic, propionic, and normal butyric acids have been studied at 20, 30, 40, and 50°. While the results found in the case of the propionate and the butyrate are in reasonable agreement with the previously published work of Evans and co-workers, the results obtained with the acetate are somewhat different.

The activation energy of this reaction appears to be the same for the ethyl esters of normal acids, the average value being 14,900 cal./mole. The changes in the reaction rate constants as the length of the carbon chain is increased must, therefore, be attributed to the " s " factor in the equation $k = sZe^{-E/RT}$.

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(7) Dippy, *J. Chem. Soc.*, 1222 (1938).