

and diethers in which the alkoxyalkyl groups are:  $\beta$ -ethoxyethyl,  $\beta$ -butoxyethyl,  $\gamma$ -ethoxypropyl and  $\gamma$ -butoxypropyl. As germicides, the monoethers are less efficient than the alkyl monoethers of analogous size.

$\omega$ -Propoxy- and  $\omega$ -butoxyresacetophenones have been prepared. The reduction of  $\omega$ -alkoxyresacetophenone to ethylresorcinol was observed to take place under the conditions of the Clemmensen reduction.

A condensation of  $\beta$ -ethoxypropionitrile with resorcinol has been found to produce  $\beta$ -(2,4-dihydroxyphenyl)-propionic acid. The reaction

does not follow the course of a typical Hoesch condensation.

$\delta$ -Methoxycrotyl bromide, synthesized from butadiene, was condensed with resorcinol to produce 4-( $\delta$ -methoxycrotyl)-resorcinol. These additional new compounds also were prepared:  $\beta$ -ethoxyethyl sulfite, butoxyacetonitrile,  $\gamma$ -butoxypropyl bromide,  $\omega$ -methoxyresacetophenone oxime, 4-ethyl-1,3-resorcinoldiacetic acid, 4- $\delta$ -methoxycrotyl-1,3-resorcinoldiacetic acid. Also, new syntheses of  $\beta$ -ethoxyethyl chloride and phenyl  $\beta$ -ethoxyethyl ether were developed.

EVANSTON, ILLINOIS

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

## Kinetics of the Catalyzed Esterification of Normal Aliphatic Acids in Methyl Alcohol

BY HILTON A. SMITH

During the period from 1895-1928, Goldschmidt<sup>1</sup> published a number of papers on the subject of esterification reactions catalyzed by acids. He demonstrated the fact that, under these conditions, the  $H^+$  ions from the catalyst form complexes with the alcohol molecules, and that esterification proceeds through interaction of the molecules of complex with the molecules of organic acid. Goldschmidt's work may be summarized briefly thus. The reaction representing the acid-catalyzed esterification of an organic acid with an alcohol is



and the rate of formation of ester is expressed by the equation

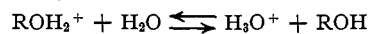
$$\frac{d(RCOOR^1)}{dt} = k(RCOOH)(R^1OH_2^+) \quad (1)$$

In dry alcohol, the concentration of alcohol complex may be considered to be equal to the total  $H^+$  concentration, or when a strong mineral acid is used as a catalyzer, equal to the concentration of such acid. The rate of formation of ester in any particular case is thus proportional to the momentary concentration of the organic acid.

However, as water is formed, it competes with the alcohol for the hydrogen ion, cutting down the concentration of alcohol complexes, and hence slowing up the esterification. An equilibrium

(1) See especially Goldschmidt and Udby, *Z. physik. Chem.*, **60**, 728 (1907); Goldschmidt and Theusen, *ibid.*, **81**, 30 (1912); Goldschmidt and Melbye, *ibid.*, **143**, 139 (1929); Goldschmidt, Haaland and Melbye, *ibid.*, **143**, 278 (1929).

is set up between alcohol and water complexes, thus



and the equilibrium constant,  $K$ , for this reaction is given by the equation

$$K = \frac{(H_3O^+)(ROH)}{(ROH_2^+)(H_2O)}$$

Since in an alcohol, (ROH) may be considered constant, a new constant,  $r$ , may be defined by the equation

$$r = \frac{(ROH)}{K} = \frac{(ROH_2^+)(H_2O)}{(H_3O^+)} \quad (2)$$

Essentially all the hydrogen ions present will be tied up as complexes with either water or alcohol molecules so that

$$(H_3O^+) = (\text{total } H^+) - (ROH_2^+) \quad (3)$$

Combining equations (2) and (3), one obtains for  $r$  the expression

$$r = \frac{(ROH_2^+)(H_2O)}{(\text{total } H^+) - (ROH_2^+)}$$

whence

$$(ROH_2^+) = \frac{r(\text{total } H^+)}{r + (H_2O)} \quad (4)$$

Substituting this value in equation (1), the rate of formation of ester is given by

$$\frac{d(RCOOR^1)}{dt} = \frac{k(RCOOH) r(\text{total } H^+)}{r + (H_2O)}, \text{ or}$$

$$\frac{dx}{dt} = \frac{kr(\text{catalyst})(a - x)}{r + x} \quad (5)$$

where  $a$  is the original concentration of organic acid,  $x$  is the concentration of ester formed after time  $t$ , and the catalyst is a strong mineral acid.

Integrating equation (5), and setting  $x = 0$  when  $t = 0$ , one obtains for  $k$  the expression

$$k = \frac{(r + a) \ln [a/(a - x)] - x}{(\text{catalyst}) r t}$$

Goldschmidt tested this equation for a number of esterification reactions at 25° and found constant values of  $k$  up to some 80 or 90% reaction; then the reverse hydrolysis reaction becomes appreciable, and the value of  $k$  falls off.

Williamson and Hinshelwood<sup>2</sup> studied the hydron catalyzed reaction of acetic acid and methyl alcohol at several temperatures. They found the activation energy to be 10,200 cal./mole as compared with a somewhat higher value found by Rolfe and Hinshelwood<sup>3</sup> for the non-catalyzed reaction. They found also that the rate of the catalyzed reaction was much slower than the rate calculated from their activation energy and the collision number, and suggested as an explanation that the presence of a third molecule was necessary in order to have a collision between a molecule of acid and a molecule of alcohol complex result in reaction.

This paper gives the results of the study of esterification kinetics of the H<sup>+</sup> catalyzed reaction of methyl alcohol with a number of straight chain organic acids.

### Experimental

**Methanol** was obtained in a pure dry state by careful fractionation of 99.5% methyl alcohol using a five-foot (1.5-meter) spiral column. The material used came over at a constant head temperature, and was apparently as dry as samples prepared by Williamson and Hinshelwood<sup>2</sup> using aluminum amalgam.<sup>4</sup> This is evidenced by the agreement of the rate constants obtained with this alcohol with those of the authors mentioned above.

**Formic acid** was prepared from the analytical reagent (89%) acid by distillation in a 5-ft. (1.5-m.) spiral fractionating column following the method of Ewins.<sup>5</sup> The pure acid melted at 8.4° and analyzed 100.0% by titration with standard base.

**Acetic acid and propionic acid** were obtained by fractionation of c. p. glacial (99.5%) acetic acid and of Eastman propionic acid in a 5-ft. (1.5-m.) spiral column. The pure acetic acid melted at 16.6°. The acetic acid

analyzed 99.9% and the propionic acid 99.8% by titration with standard base.

***n*-Butyric acid, *n*-valeric acid, and *n*-caproic acid** were obtained by fractionation of the Eastman acids in a 5-ft. (1.5-m.) Vigreux type column. The resulting products analyzed as follows: butyric, 99.7%; valeric, 99.9%; caproic, 99.2%.

***n*-Pelargonic acid** as obtained from the Eastman Kodak Co. analyzed 99.4% with standard base and melted at 11.6°. No further purification was attempted.

The general method was quite simple. Pure dry hydrogen chloride was passed into dry methanol. The concentration of the hydrochloric acid was then found by titration with standard base, and subsequently adjusted to the desired value by dilution with more pure alcohol. While such solutions were found to be stable over a considerable period, they were always freshly prepared.

Glass-stoppered bottles containing this solution were placed in electrically controlled water thermostats which gave temperatures constant to ±0.01°. When temperature equilibrium had been established, the calculated amount of organic acid was added to the alcohol, and, after thorough mixing, the reaction was followed by a

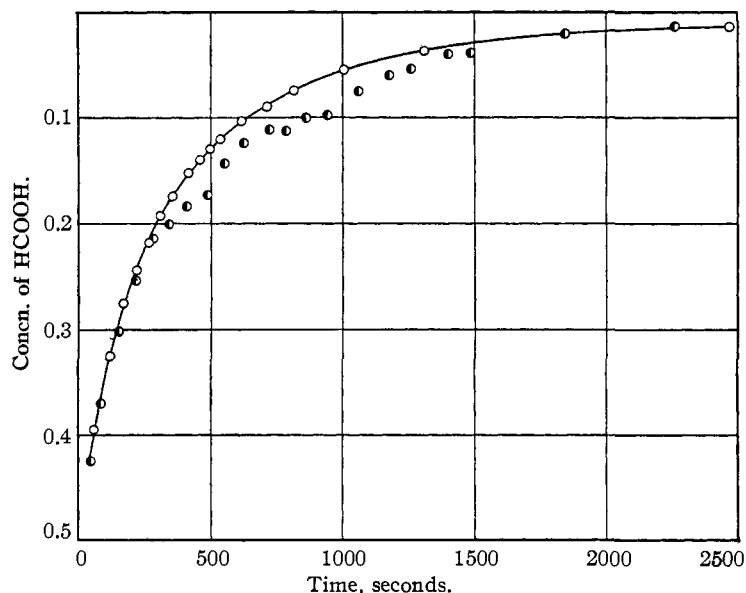


Fig. 1.—Rate of esterification of HCOOH in CH<sub>3</sub>OH catalyzed by HCl. Initial concn. HCOOH, 0.5 M. Concn. HCl, 0.005 M. ○, points obtained when following reaction with alcoholic KOH; ●, points obtained when following reaction with aqueous KOH.

simple titration method using standard potassium hydroxide and phenolphthalein indicator.

In the case of formic acid, titration with a water solution of potassium hydroxide gave very erratic results. This evidently was due to the extreme rapidity of hydrolysis of the methyl formate formed in the course of the reaction. This difficulty was overcome by using a standard solution of potassium hydroxide dissolved in absolute methanol with brom cresol purple as the indicator. Figure 1 shows a comparison of the two methods of analysis for formic acid and methanol at 30° using 0.005 N hydro-

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

(3) Rolfe and Hinshelwood, *ibid.*, **30**, 935 (1934).

(4) Hartley and Raikes, *J. Chem. Soc.*, **127**, 524 (1925).

(5) Ewins, *ibid.*, **105**, 350 (1914).

chloric acid as catalyst. The same type of result was obtained in all cases tried.

### Experimental Results and Calculations

The results of a typical run are given in Table I. Here  $k^1$  represents the rate constant as calculated from the simple unimolecular expression

$$k^1 = \frac{2.303 \log a/(a-x)}{(\text{catalyst})t}$$

and  $k$  represents the constant calculated from Goldschmidt's formula. The units of  $k^1$  and  $k$  are liters/mole  $\times$  sec. The table demonstrates the constancy of  $k$  as compared to  $k^1$ .

TABLE I  
ESTERIFICATION OF  $\text{CH}_3\text{OH}$  AND  $\text{CH}_3\text{COOH}$  AT  $50^\circ$   
 $a = 0.5$ , (HCl catalyst) = 0.005

$t$ , min.	$(a-x)$	$k^1$	$k$
1	0.467	0.228	0.236
5.5	.365	.191	.224
9	.308	.180	.224
16.75	.223	.161	.221
24.5	.170	.147	.215
38.5	.110	.130	.207

The above values are representative of 16 measurements, all of which give values of  $k$  between 0.236 and 0.207.

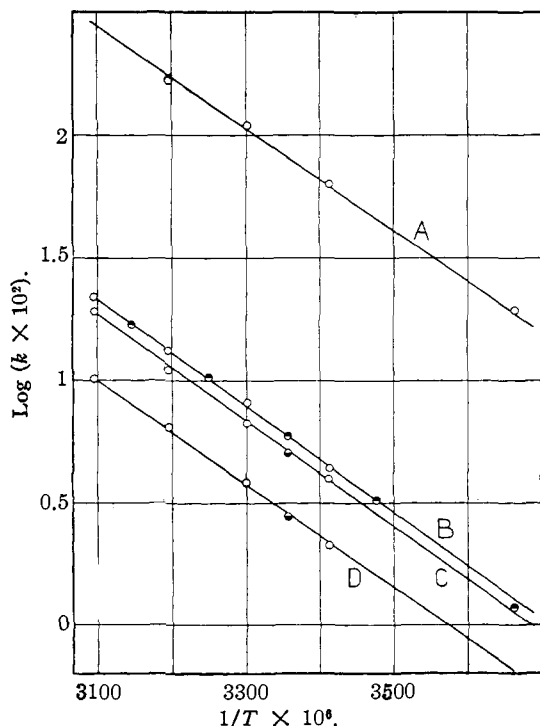


Fig. 2.—Temperature coefficients of hydrogen ion catalyzed esterification of  $n$ -alkyl acids in methyl alcohol: A, formic acid; B, acetic acid; C, propionic acid; D, all higher acids;  $\circ$ , points obtained by Smith;  $\bullet$ , points obtained by Williamson and Hinshelwood<sup>6</sup>;  $\ominus$ , points obtained by Goldschmidt and Thuesen<sup>6</sup>.

The values of  $r$  in the expression for  $k$  were obtained by substituting two values of  $t$  with the corresponding  $x$  values in the expression for  $k$ , setting the two expressions thus obtained equal to each other and solving for  $r$ . This was done for all the acids, and the values of  $r$  were found to be the same for each temperature irrespective of the acid used. This would be expected from the definition of  $r$  (see equation 2). The values at each temperature were averaged, and this average value used in all calculations. The variation in  $r$  is of the same order as that found by Williamson and Hinshelwood<sup>2</sup> in the case of acetic acid and methyl alcohol. These values are given in Table II.

TABLE II  
INFLUENCE OF TEMPERATURE ON  $r$

$t$ , $^\circ\text{C}$ .	0	20	30	40	50
$r$	0.11	0.20	0.25	0.32	0.42

Table III shows the values of  $k$  for  $\text{H}^+$  catalyzed esterification of the seven acids studied in methyl alcohol. Since, in the early stages of the reaction, experimental errors are large and, in the later stages, the values of  $k$  fall off due to the reverse hydrolysis reaction, the values given here were calculated by averaging the individual figures obtained during 20–80% reaction. The number of values averaged was generally around ten for each run. The  $\pm$  errors are given to indicate that in no case was the falling off of  $k$  very appreciable. In all cases the initial concentration of organic acid was adjusted to 0.500 mole per liter and that of the hydrochloric acid catalyst to 0.005 molar.

Figure 2 shows the plot of  $\log K$  against  $1/T$  for the acids studied. All acids having more than three carbon atoms are represented by one line. The values of  $k$  for such acids were averaged for the purpose of making this plot. The points obtained by Goldschmidt and Thuesen<sup>6</sup> at a temperature of  $25^\circ$  and those obtained by Williamson and Hinshelwood for acetic acid show excellent agreement with those reported here, thus indicating that the methanol dried by fractionation was as satisfactory as that dried by distillation from metallic calcium or by distillation from aluminum amalgam.

The slopes of the four lines shown in Fig. 2 are the same (within the limits of experimental error), and the calculated value of the activation energy

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

TABLE III  
REACTION RATE CONSTANTS FOR ESTERIFICATION OF NORMAL ALIPHATIC ACIDS IN METHYL ALCOHOL CATALYZED BY H<sup>+</sup> IONS

In all cases  $a = 0.500$ ,  $(\text{HCl}) = 0.005$

Acid	$t = 20^\circ$	$= 30^\circ$	$k$	$t = 40^\circ$	$= 50^\circ$
Formic	0.647 $\pm$ 0.020 .618 $\pm$ .013	1.08 $\pm$ 0.01 1.12 $\pm$ .03		1.74 $\pm$ 0.02 1.71 $\pm$ .01	
Av.	.632	1.10		1.73	
Acetic	.0440 $\pm$ .0009 .0439 $\pm$ .0007	0.0811 $\pm$ .0010 .0816 $\pm$ .0013		0.131 $\pm$ .002 .132 $\pm$ .001	0.219 $\pm$ 0.003 .219 $\pm$ .004
Av.	.0440	.0814		.132	.219
Propionic	.0403 $\pm$ .0005 .0397 $\pm$ .0005	.0667 $\pm$ .0008 .0672 $\pm$ .0014		.111 $\pm$ .002 .111 $\pm$ .006	.190 $\pm$ .009 .195 $\pm$ .005
Av.	.0400	.0670		.111	.193
Butyric	.0211 $\pm$ .0002 .0211 $\pm$ .0002	.0368 $\pm$ .0004 .0375 $\pm$ .0004		.0653 $\pm$ .0007 .0652 $\pm$ .0010	.103 $\pm$ .003 .103 $\pm$ .005
Av.	.0211	.0372		.0652	.103
Valeric	.0214 $\pm$ .0003 .0214 $\pm$ .0002	.0399 $\pm$ .0009 .0405 $\pm$ .0009		.0648 $\pm$ .0004 .0666 $\pm$ .0020	.100 $\pm$ .005 .102 $\pm$ .003
Av.	.0214	.0402		.0657	.101
Caproic	.0220 $\pm$ .0004 .0219 $\pm$ .0007	.0395 $\pm$ .0008 .0388 $\pm$ .0009		.0657 $\pm$ .0015 .0651 $\pm$ .0016	.103 $\pm$ .004 .101 $\pm$ .003
Av.	.0219	.0391		.0654	.102
Pelargonic	.0211 $\pm$ .0005 .0210 $\pm$ .0004	.0389 $\pm$ .0008 .0371 $\pm$ .0003		.0654 $\pm$ .0020 .0649 $\pm$ .0007	.101 $\pm$ .003 .099 $\pm$ .002
Av.	.0211	.0380		.0652	.100
	$t = 0^\circ$				
Formic	.182 $\pm$ .003 .187 $\pm$ .005				
Av.	.184				

comes out to be 10,000 cal./mole. The value found by Williamson and Hinshelwood<sup>2</sup> was 10,200 cal./mole. Table IV gives the values of  $k$  for the acids studied when the exponential term has been included.

Acid	$k$
Formic	$1.7 \times 10^7 e^{-10,000/RT}$
Acetic	$1.2 \times 10^6 e^{-10,000/RT}$
Propionic	$1.0 \times 10^6 e^{-10,000/RT}$
Butyric and higher	$5.7 \times 10^6 e^{-10,000/RT}$

### Discussion

A consideration of the reaction velocity constants for the catalyzed reactions of straight chain acids with methyl alcohol shows that, since the activation energy is the same in all cases, the variation of the  $k$ 's must be entirely due to the  $A$  factor in the equation

$$k = Ae^{-E/RT} = sZe^{-E/RT}$$

The values of  $k$  and hence of the  $A$  factor, decrease with increasing chain length from formic to butyric acid. Further increase in the chain length has no effect. This was demonstrated here for chain lengths up to 9 carbon atoms. Indication that still further lengthening of the

carbon chain does not change the value of  $k$  may be seen from the fact that at 25° Goldschmidt<sup>6</sup> found the same reaction rate for butyric and lauric acids (12 carbon atoms).

The difference between the constants for formic, acetic, propionic, and butyric acids is not at all regular. The value of  $k$  drops greatly for an increase from 1 to 2 carbon atoms, drops very little from 2 to 3 carbon atoms, and then has a larger drop when a fourth carbon atom is added to the chain.

Theoretically the  $A$  factor may be compared with the collision number  $Z$  as given by the equation

$$Z = N_1 N_2 \sigma_{1,2}^2 8RT(1/M_1 + 1/M_2)$$

Williamson and Hinshelwood<sup>2</sup> found that the value of the  $Z$  was  $10^6$  times as great as  $A$  for the case of the reaction of acetic acid with methyl alcohol. They suggested that part of this difference might be accounted for by the necessity of the presence of a third molecule at the time of collision of a molecule of acid and alcohol complex, if reaction is to ensue. This conclusion does not seem logical. The reaction is of an exchange type, and should require no stabilization

by a third molecule. Furthermore, the necessity of triple collisions does not aid in explaining the variation of  $A$  with increasing chain length. It seems more reasonable to assume that the difference between  $A$  and the calculated value of  $Z$  is due entirely to the steric factor,  $s$ , which may indicate the necessity of the alcohol and acid molecules being oriented in some particular fashion when they collide, that the carboxyl group must be in some particular state of resonance when collision occurs if reaction is to follow, or that all of the activated complexes formed at the time of collision do not break up to form ester and water, but a large share may revert to the acid and alcohol molecules. This latter explanation is perhaps the most likely.

The variation of  $Z$  with increasing chain length may be estimated readily. The concentrations of alcohol complex and acid molecules ( $N_1$  and  $N_2$ ) remain the same for all cases. The diameter of the complex ( $\sigma_1$ ) will remain the same. In place of the diameter of the acid molecule ( $\sigma_2$ ) the diameter of the carboxyl group of the molecule may be substituted since reaction can occur only when the alcohol complex is in collision with this part of the acid molecule. The calculated variation in  $Z$  and the actual variation in  $A$ , assuming in both cases the value of unity for formic acid, is given in Table V.

TABLE V

Acid	Mol. wt.	$Z$	$A$
Formic	46	1	1
Acetic	60	0.905	0.0726
Propionic	74	.846	.0629
Butyric	88	.805	.0353
Valeric	102	.775	.0353
Caproic	116	.745	.0353
Pelargonic	158	.711	.0353

This table indicates that the change in  $Z$  is not at all comparable to the variation in the  $A$  factor, and some other explanation must be given. Another interesting point in the table is that, while the  $A$  factor remains constant for acids higher than propionic, the  $Z$  factor drops by more than 10% from butyric to pelargonic acid. Such a drop should be readily detectable in  $A$  unless the steric factor ( $s$ ) changes in such a manner as to keep  $A$  constant with varying  $Z$ . This seems improbable. It seems more logical to assume that both  $s$  and  $Z$  remain constant. This would be true for  $Z$  if the acid molecules were considered to be almost stationary as compared to the movement of the complex molecules.

It is apparent that if the foregoing ideas are correct, the variation in  $k$  with increasing chain length must be due almost entirely to changes in the  $s$  factor. This may be at least qualitatively explained by examination of the structure of the acid molecules.

In the case of formic acid, alcohol complex molecules may collide with the carboxyl group if they approach the acid molecule from almost any angle. However, in acetic acid, the methyl group will screen the carboxyl group in such a manner that alcohol complexes can approach from a limited direction only. Hence the reaction rate will be considerably lessened. The addition of another methyl group to form propionic acid will actually have only a little further effect on the rate of reaction since the ethyl group screens the carboxyl group little more than does the methyl group.

Still further lengthening of the carbon chain would give no more screening of the carboxyl group were the chain of the simple zig-zag character. However, if the next methyl group tends to form a ring, it will have a considerable screening effect, causing a greater difference between the reaction velocity constants of propionic and butyric acids than that between acetic and propionic acids. This is actually the case. Further lengthening of the carbon chain will have little effect on  $k$  since further ring formation is not possible. This readily may be seen with the aid of molecular models.

Goldschmidt<sup>6</sup> also found the value of  $k$  at 25° for phenylacetic acid to be the same as that for butyric acid. This is explained readily on the basis of the theory suggested above. By necessity the phenyl group must tend to form a ring of the type suggested for butyric acid, and it will have exactly the same screening effect as butyric and higher acids. This type of ring formation for butyric acid has been postulated to explain the abnormally high dissociation constant of butyric acid.<sup>7</sup>

It is possible that the variation in the  $s$  factor may be due to dissimilarities in the activated complexes formed when different acids are used. This may, indeed, be the explanation for the fact that the change in esterification rate when one substitutes acetic acid for formic acid is so great. It does not seem reasonable, however, to assume that the complexes formed from acetic, propionic,

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

and butyric acids would be sufficiently different to cause the observed variation in the rate constants. If, however, the variation in  $k$  is due to differences in the activated complexes, these complexes can be different only because the acids themselves differ. One thus ends up with the necessity of falling back on the structure of the acids themselves in order to explain the observations.

Hinshelwood and Legard<sup>8</sup> state in the conclusions of their paper on the factors determining the velocity of esterification of carboxylic acids in solutions, that for a series of acids, "those which react most slowly correspond to the highest values of  $E$ ," and that "steric hindrance appears to depend upon high activation energy rather than to be of a purely geometrical character." The results obtained for the series of normal carboxylic acids seem to be at variance with their conclusions. Since the values of  $E$  are the same in all cases, the slower reactions cannot be due to higher activation energies, and the steric hindrance encountered in this series must be explained in some other manner. If the carbon chain near the carboxyl group is of a ring rather than a straight chain structure, this steric hindrance may be almost completely explained by geometrical considerations. The conclusions of Hinshelwood and Legard undoubtedly are correct for the type of series which they considered, namely, a series representing increased substitution in the  $\alpha$ -position. However, their results cannot be applied to a different type of series such as that considered here.

General confirmation of the results here reported is found in three articles by Evans and co-workers. The first of these<sup>9</sup> reports the study of the influence of alkyl groups on the acid catalyzed prototropy of phenyl alkyl ketones. The second<sup>10</sup> deals with the same reaction catalyzed by base, and the third<sup>11</sup> reports the study of the influence of alkyl groups upon the velocity of saponification of saturated aliphatic esters. The results of these three papers indicate the fact that in these reactions also all normal alkyls from propyl on up have the same effect on the reaction velocities.

However, the authors draw several conclusions which do not necessarily follow from their ex-

periments. They state, for instance, that "in esters which are not branched at the  $\alpha$  carbon atom, the changes in velocity are due almost entirely to changes in  $E$ ," and also that " $E$  increases gradually as the normal series is ascended and tends to reach a constant maximum." At 25°, their values of  $k \times 10^8$  for the saponification of the ethyl ester of various normal acids are: acetic 6.21, propionic 3.63, butyric 1.72, valeric 1.92, hexoic 2.07, heptoic 1.79, and octoic 1.84. The values which they give for the corresponding activation energies are: acetic 14,200, propionic 14,500, butyric 15,000, valeric 14,700, hexoic 14,800, heptoic 15,000, and octoic 15,000. If the authors feel that the 300 cal. increase in the activation energy from ethyl acetate to ethyl propionate is significant, thus accounting for the drop in  $k$  from 6.21 to 3.63, how do they explain the fact that the 300 cal. decrease which takes place between ethyl butyrate and ethyl valerate has essentially no effect on  $k$ ? It would seem that, with the possible exception of the values dealing with ethyl acetate, all of these values of  $k$  are the same within experimental error. Unfortunately insufficient data are given to allow any reasonable estimate of this error. Furthermore, the only indication of purity of their compounds is a list of the boiling points which are, with one exception, given only to the nearest whole degree.

Further work, using substituted acids and other alcohols than methanol, is now in progress; the results should aid further in clearing up the question of the effect of alkyl groups on the rate of esterification reactions.

### Summary

The kinetics of the hydrogen ion catalyzed esterification of seven normal organic acids in methyl alcohol have been studied. The activation energy is 10,000 cal./mole in all cases. The values of the rate constants are

Acid	$k$ (liters/mole $\times$ sec.)
Formic	$1.7 \times 10^7 e^{-10,000/RT}$
Acetic	$1.2 \times 10^6 e^{-10,000/RT}$
Propionic	$1.0 \times 10^6 e^{-10,000/RT}$
All higher normal acids	$5.7 \times 10^6 e^{-10,000/RT}$

The influence of the length of the carbon chain of the acid upon the rate of its esterification has been shown to be due almost entirely to the  $s$  factor in the equation  $k = sZe^{-E/RT}$ . The variation may be explained at least qualitatively on

(8) Hinshelwood and Legard, *J. Chem. Soc.*, 587 (1935).

(9) Evans, *ibid.*, 785 (1936).

(10) Evans and Gordon, *ibid.*, 1434 (1938).

(11) Evans, Gordon and Watson, *ibid.*, 1439 (1938).

the assumption that the carbon chain of the lower acids tends to have a ring rather than a straight chain structure.

BETHLEHEM, PENNA. RECEIVED NOVEMBER 22, 1938

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

## The Heats of Solution and of Dilution of the Binary Systems Zinc Nitrate-Water and Cadmium Nitrate-Water

BY WARREN W. EWING, JOHN D. BRANDNER AND WALTER R. F. GUYER

This article, which presents calorimetric data for the binary systems zinc nitrate-water and cadmium nitrate-water, is a continuation of a series of studies made on the nitrates of certain bivalent metals. Vapor pressure studies of these two systems already have been published.<sup>1,2</sup> These two systems are excellent for these studies since the salts form several hydrates which melt not far above room temperature, their anhydrides are extremely soluble, and the solutions can be supercooled.

Solubility studies<sup>3-5</sup> show that zinc nitrate crystallizes in five hydrated forms, namely,  $\text{Zn}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$  (T. P.  $-17.6^\circ$ ),  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (m. p.  $36.1^\circ$ ),  $\text{Zn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (m. p.  $44.7^\circ$ ),  $\text{Zn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (m. p.  $55.4^\circ$ ), and  $\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  (m. p.  $73.9^\circ$ ). Zinc nitrate anhydride has also been prepared as will be shown later in this article. Likewise, cadmium nitrate<sup>6,7</sup> exists as the anhydride and forms three hydrates, namely,  $\text{Cd}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$  (T. P.  $+3.5^\circ$ ),  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (m. p.  $59.5^\circ$ ) and  $\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  (m. p.  $56.8^\circ$ ).

The stable saturated solution of the monohydrate of zinc nitrate has a concentration of 86.2% at  $51.8^\circ$  and the anhydride of cadmium nitrate, 86.0% at  $56.8^\circ$ . Since solutions of these salts can be supercooled to room temperature, this means that calorimetric measurements can be obtained at  $25^\circ$  through extremely large concentration ranges: up to 35 molal for zinc nitrate and up to 21 molal for cadmium nitrate. The zinc nitrate solutions decompose slowly at the very high concentrations but suitable precautions enable measurements to be made with a reasonable degree of accuracy. The calorimetric data presented consist of heats of solution of the various hydrates and the anhydrides and heats of

dilution of solutions of various concentrations. These data were obtained by sealing the various samples in small bulbs and then breaking the bulbs under water in an adiabatic calorimeter, to yield dilute solutions.

### Preparation of Materials

Zinc nitrate hexahydrate was prepared by recrystallizing the c. p. salt three times from a slightly acidified solution. The moist product was dried in a stream of air on a day when the humidity was low. The tetrahydrate, dihydrate and monohydrate were prepared by melting the purified hexahydrate and evaporating to the required concentration. The solution was then slightly acidified, the desired crystallization was carried out, and the hydrates were filtered on sintered glass filters at temperatures slightly above the respective eutectic temperatures. The excess of nitric acid was removed by evaporation in a vacuum and the final drying carried out in vacuum desiccators over the proper drying agents, *viz.*, 65% sulfuric acid for the tetrahydrate, 78% sulfuric acid for the dihydrate and phosphorus pentoxide for the monohydrate.

The preparation of anhydrous zinc nitrate offered extreme difficulties. The dehydration of the monohydrate either by heating or by continuous evacuation by means of a mercury diffusion vacuum pump at room temperatures resulted in a decomposition of the nitrate. An insoluble product was formed probably consisting of various basic zinc nitrates.<sup>8,9</sup> Success was finally attained by the reaction of nitrogen pentoxide on U. S. P. zinc oxide. Ozone was used to inhibit the slow decomposition of the nitrogen pentoxide.<sup>10,11</sup> The apparatus consisted of an all-glass system in which the gases were circulated by means of a pump in a cyclic manner. The successive parts of the cycle consisted of the nitrogen pentoxide generator, phosphorus pentoxide drying tube, eight zinc oxide reaction bulbs, phosphorus pentoxide drying tube cold trap, pump, ozonizer, nitrogen pentoxide generator, etc. The zinc oxide bulbs were blown in such a manner that the two arms were above the axis of the bulb so that the nitrogen pentoxide could circulate over the surface of the zinc oxide. The bulbs were of such a size that they could be sealed and used in the calorimeter.

The zinc oxide was first dried by passing oxygen through the system for several hours. Even this treatment does

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