THE ESTERIFICATION KINETICS OF ACETIC ACID AND *n*-PROPYL ALCOHOL USING A GAS CHROMATOGRAPH

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Introduction

Recently, gas chromatography has been suggested as a tool for following the course of chemical reactions in order to obtain information concerning reaction kinetics (Drew and McNesby, 1957; Greene, 1957; and Hatch, 1958). Most references allude only to gas phase reactions, although Hatch mentions an isomerization reaction at 40°. A great advantage of this application of gas chromatography is that starting materials of great purity are not necessary. The conventional method for determining the amount of a substance in a quantitative manner involves the determination of either the area or the height of the chromatographic peak (Strobel, 1960, p. 447). The present authors have found that in the reaction studied, it is convenient to use a calibration method relating the product ester peak height to the concentrations of reactants in the reaction mixture.

Gas chromatographic technique is illustrated by a study of the kinetics of the esterification of *n*-propyl alcohol with acetic acid in a non-aqueous system without the addition of a catalyst. The reaction was studied at temperatures between 25 and 45°, well below the operating temperature of the gas chromatograph. In addition to testing the analytical method described, further information was sought concerning the relative importance in this type of a mixture of catalysis due to protons and that due to undissociated acetic acid.

Experimental

Apparatus. A Perkin-Elmer, Model 154C vapor fractometer was used for all experimental measurements. A column inlet pressure of two atmospheres and an outlet pressure of one atmosphere, within the limits of daily atmospheric pressure variations, were maintained. The temperature of the column and detector was maintained at 90° ± 0.5°. A flow rate of 35 ml. of helium per minute was employed. The detector unit was operated at 8.0 volts, with a recording sensitivity setting of 8. A Perkin-Elmer micro dipper sample introduction assembly and a 0.002 ml. micro dipper were used to introduce sample aliquots.

Bronwill and Freas Model L-2 stationary water baths were used for controlling the temperatures of the reaction mixtures.

Reagents. The reagents used were DuPont reagent grade glacial acetic acid, Fisher Certified reagent grade *n*-propyl alcohol and *n*-propyl acetate. In all cases, commercially available reagents were used without further purification.

Calibration Curve. The calibration curve was prepared from chromatographic measurements made on various synthetic mixtures of distilled water, *n*-propyl alcohol, glacial acetic acid, and *n*-propyl acetate. The height of the ester peak, meas-

ured from the base line of the chromatogram, was determined and plotted *vs.* concentration of ester present. The data from these measurements are shown in Table I; the linear calibration plot obtained is shown in Figure 1.

Esterification Mixtures. Reaction mixtures containing excess acid, excess alcohol, and equal concentrations, respectively, were prepared in 50-ml. glass-stoppered volumetric flasks. The respective volumes of acid and alcohol were accurately measured with a calibrated buret. These mixtures were maintained at the desired constant temperature, and gas chromatograms were recorded for aliquot samples of each mixture at various time intervals throughout the course of the esterification. The concentrations of ester produced were determined from the calibration plot. In order to determine the effect of reaction temperature on the reaction rate, the reaction mixtures were measured at three different temperatures. The data obtained from such measurements are shown in Table II.

TABLE I.

Calibration Data for *n*-Propyl Acetate in Mixtures of *n*-Propyl Alcohol, Glacial Acetic Acid, Water, and the Ester.

Ester *Present* moles/liter	Ester *Peak Height* divisions
0.0	1.0
1.27	12.8
1.89	19.5
2.64	27.6
3.77	37.5

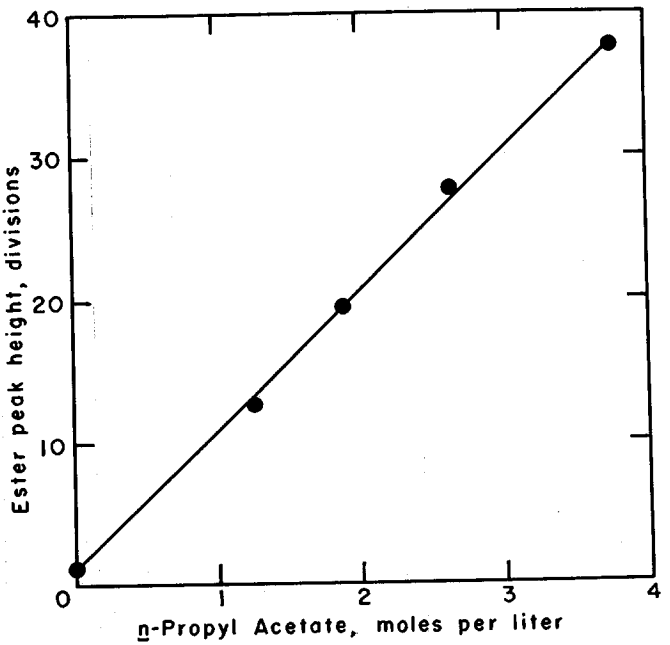

Fig. 1.—Gas chromatograph calibration curve for *n*-propyl acetate in esterification reaction mixtures.

TABLE II.—Kinetic Data for the *n*-Propyl Alcohol-Acetic Acid Esterification.

Initial Concentrations		Reaction Temperature	Reaction Time	*n*-Propyl Acetate Produced
Acetic Acid	*n*-Propyl Alcohol			
moles/liter	moles/liter	°C	Hours	moles/liter
7.58	7.58	28	0	0
			24	0.100
			48	0.350
			78	0.500
			96	0.700
			168	1.175
			216	1.400
		35	0	0
			24	0.400
			72	1.050
			101	1.325
			124	1.525
			144	1.675
			168	1.950
			216	2.350
			240	2.450
		45	21	0.750
			49	1.425
			72	1.800
			95	2.250
			118	2.575
12.18	4.06	28	0	0
			24	0.150
			48	0.350
			72	0.500
			96	0.675
			168	1.100
			216	1.325
		35	0	0
			50	0.650
			72	0.975
			100	1.250
			123	1.475
			144	1.625
			168	1.900
			216	2.200
			240	2.350
		45	22	0.710
			51	1.400
			72	1.850
			96	2.250
			120	2.525
3.54	10.62	25	168	0.500
			216	0.600

TABLE II.—Continued.

Initial Concentrations		Reaction Temperature	Reaction Time	*n*-Propyl Acetate Produced
Acetic Acid	*n*-Propyl Alcohol			
moles/liter	moles/liter	°C	Hours	moles/liter
			264	0.675
			336	0.750
			384	0.875
			432	0.925
			504	1.025
			552	1.075
			600	1.150
			672	1.275
		35	48	0.300
			72	0.400
			120	0.625
			144	0.700
			168	0.875
			216	1.000
		45	24	0.300
			52	0.615
			72	0.830
			96	1.025
			120	1.175

Measurement Procedure. Each experimental measurement was made employing the following procedure. The micro dipper was cleaned with acetone and dried with air. The tip was immersed in the reaction mixture, allowing the dipper to fill by capillary action. The dipper was then removed from the reaction mixture, dried, inspected visually to ensure that it was full, and inserted into the introduction system for sufficient time to complete the transfer of the sample into the column.

RESULTS

The concentration of the *n*-propyl acetate was determined from the calibration curve described in the previous section. The ester concentrations in these solutions varied from 0.00 *M* to 3.77 *M*. From the ester concentration, the initial compositions and the stoichiometry, the concentrations of the other components were determined. Initial reaction mixtures of three types were investigated: (CH_3COOH: *n*-C_3H_7OH in moles/liter) 3:1, 1:1, 1:3. Measurements were made at three reaction temperatures between 25° and 45°.

In order to test whether the data obtained in the experiment obeyed a certain rate expression, numerous plots of the general type shown in Figures 2, 3, and 4 were made. The abscissa was chosen in each case so as to obtain a linear plot for the correct rate expression. Contrary to

TABLE III.—Specific Rates, Type of Equation Applicable and F-Test Values as Determined by Different Kinetic Equations.

Mixtures	28 °C Equation (2) kx10⁴	Polynomial Applicable	F Value	28 °C Equation (3) kx10⁴	Polynomial Applicable	F Value	28 °C Equation (4) kx10⁴	Polynomial Applicable	F Value
(acid:alcohol) 3:1	0.07	Linear	19	1.62	Linear	93	4.73	Linear	431
1:1	0.21	Linear	851	1.45	Linear	1084	1.64	Linear	859
1:3	0.64	Linear	1410	55.30	Quadratic	1004	1.99	Linear	507
	35 °C			35 °C			35 °C		
3:1	0.19	Linear	325	3.38	Linear	4619	18.31	Quadratic	191
1:1	0.43	Linear	1454	2.64	Linear	2906	3.63	Linear	622
1:3	1.49	Linear	547	1.56	Linear	67	4.14	Linear	410
	45 °C			45 °C			45 °C		
3:1	2.61	Quadratic	357	7.68	Linear	5947	36.99	.....	
1:1	0.94	Linear	1187	5.68	Linear	1937	7.98	Linear	451
1:3	3.40	Quatric	135,737[1]	3.49	Linear	1601	10.06	Linear	691

[1] The F-test for the linear polynomial gave a value of 7320.

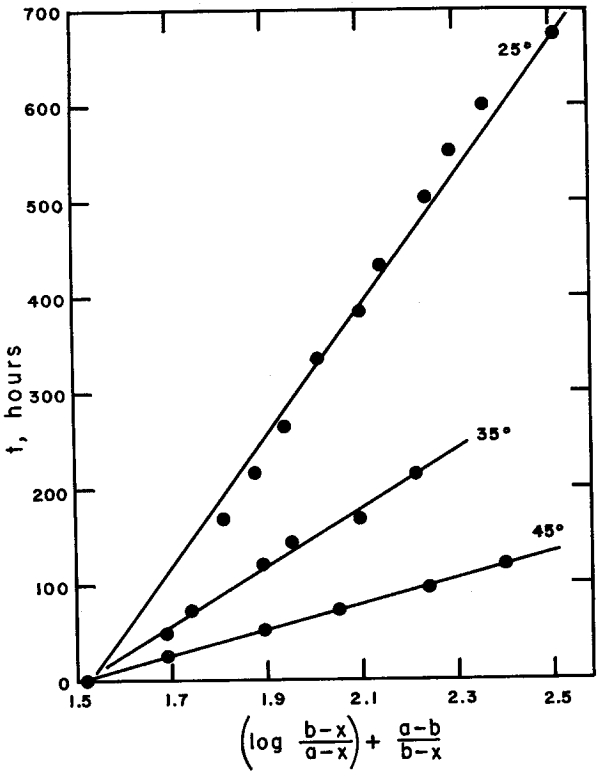

Fig. 2.—Representative kinetic plots used to determine k from equation (2).

expectations, several rate expressions appeared to be equally valid, as indicated by the linearity of the plots.

A Least Squares Procedure was then used to determine the polynomial fit to each set of points plotted. The highest degree polynomial tested was a quatric. An F-test (Dixon and Massey, 1951, p. 178: the larger the F-value, the better the fit) was used to determine the degree of "goodness". The calculations were performed on an IBM 650 computer using a program developed by the University of Florida (1958). The results are summarized in Table III.

The final values of k were not corrected for volume expansion inasmuch as the temperature range was only 20°.

Figure 5 shows a plot, for each mixture, of the logarithm of the rate constants *vs.* the reciprocal of the absolute temperature. The Arrhenius activation energy was determined from the slopes and found to be 16 ± 0.6 kcal. mole^{-1} for each mixture.

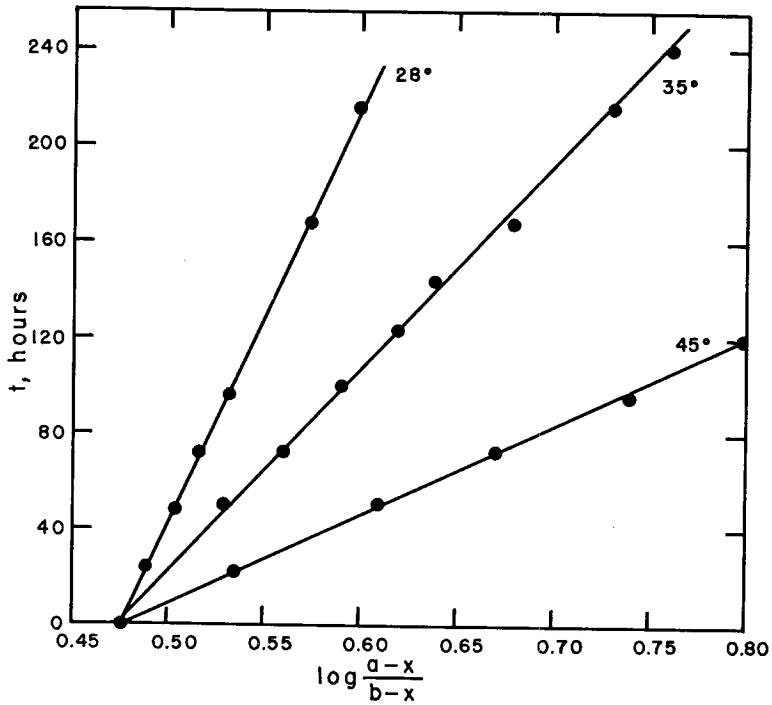

Fig. 3.—Representative kinetic plots used to determine k from equation (3).

Discussion

The kinetics of non-catalyzed (no specific catalyst added) esterification have been investigated extensively. Rolfe and Hinshelwood (1934) have shown that the rate expression for the disappearance of acetic acid in a methyl alcohol solvent is given by equation 1.

The acid catalysis is indicated by $[H^+]$. The term $[CH_3OH]$ is indicated as a constant because the methyl alcohol was used as a solvent. These authors have shown that

$$(1) \quad -\frac{d[CH_3COOH]}{dt} = [CH_3OH] \times \left\{ k_0[CH_3COOH]\,[H^+] + k_1[CH_3COOH]^2 + k_2 \right\}$$

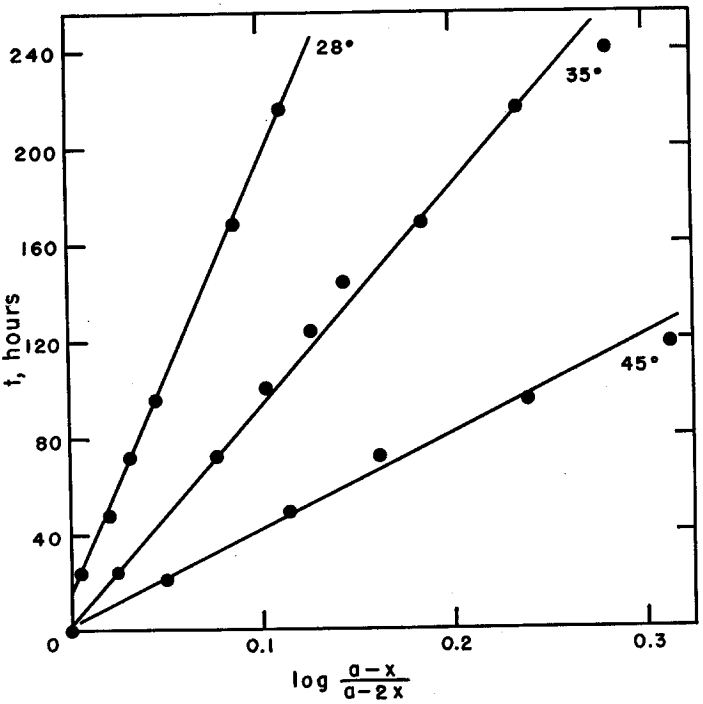

Fig. 4.—Representative kinetic plots used to determine k from equation (4).

in solutions containing acetic acid in concentrations of about one normal, the term involving k_1 dominates the term containing k_2. The term involving k_2 becomes important in solutions containing acetic acid in concentrations less than $(1/20)N$. Rolfe and Hinshelwood have also shown that the temperature coefficient of k_0 is much smaller than k_1. Thus the term involving k_0 is less important above 70°.

In the present work, the concentration of acetic acid varied between 3.6 N and 12.2 N. Under these conditions, no significant contribution from the term involving k_2 would be expected. Thus, catalysis by some basic substance (*e.g.*, $C_3H_7O^-$) is precluded as a predominant effect.

The concentration of *n*-propyl alcohol in the mixtures used is not sufficiently great (in relation to the second component of the mixture) to be considered a constant in the rate equation. Furthermore, the $[H^+]$ in these concentrations is very small. Indeed, this small value of $[H^+]$ would appear to be more important than the contribution from a term of the type indicated by k_0. Therefore, under the conditions of the present work, one might expect that the rate expression could be given by equation 2.

$$(2)\quad -\frac{d[CH_3COOH]}{dt} = k_1[CH_3COOH]^2[C_3H_7OH]$$

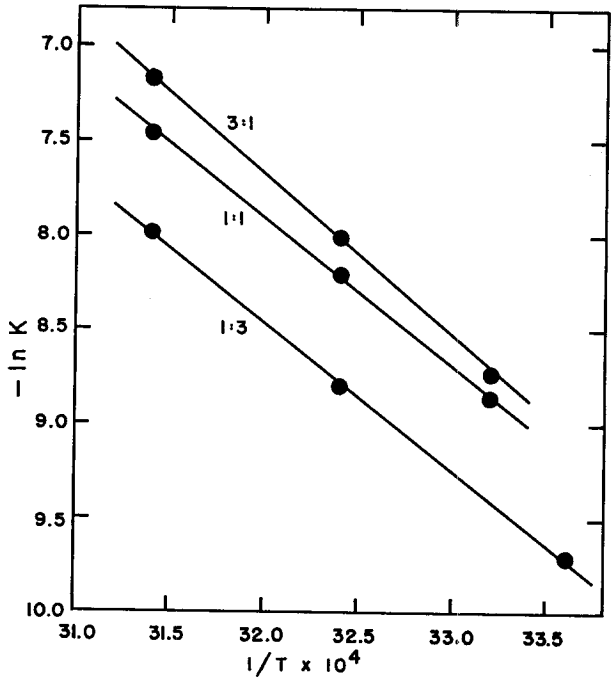

Fig. 5.—Arrhenius plots used to evaluate activation energy.

This rate expression indicates a mechanism whereby the undissociated acid molecule could catalyze the esterification. The corresponding chemical equation is

$$CH_3COOH + C_3H_7OH \xrightarrow{CH_3COOH} CH_3COOC_3H_7 + H_2O.$$

A bimolecular rate expression, shown by equation 3, has been found by Rolfe and Hinshelwood (as well as by others) for non-catalyzed esterification, under conditions similar to those of the present work (National Bureau of Standards, 1951).

$$(3) \quad -\frac{d[CH_3COOH]}{dt} = k[C_3H_7OH]\,[CH_3COOH]$$

Here again the predominant catalysis was by single molecules of undissociated acetic acid. However, the catalytic acetic acid was essentially constant, giving a pseudo-second order reaction since

$$k_1[CH_3COOH] = k$$

The actual measurement in the gas chromatograph was an expression of the vapor phase of the different molecules. It is probable that the acetic acid was in dimeric form

in the chromatographic column. If these dimeric molecules had become rate controlling, the bimolecular rate expression would be given by equation 4.

$$(4) \quad -\frac{d[CH_3COOH]}{dt} = k_1[C_3H_7OH][(CH_3COOH)_2]$$

The chemical equation for this process is

$$(CH_3COOH)_2 + 2C_3H_7OH \xrightarrow{(CH_3COOH)_2} 2CH_3COOC_3H_7 + 2H_2O$$

Only 5 of the 27 plots were found to fit a non-linear equation. The use of the F-test indicated that the rate expression for the 3:1 and 1:1 mixtures (acid: alcohol) was best described by equation 3. The difference in rate expressions may be explained in that the concentration of the catalytic molecules must take part in any reaction and then be regenerated. When there was not a great excess of acetic acid in the solution, the rate became sensitive to the change in all acetic acid taking part in the reaction.

It is interesting to note that the value of k as determined from equation 2 is essentially the same as that determined from equation 3 for the 1:3 mixture. This might indicate that the evaluation of k from equation 2 and equation 3 is equally valid for the 1:3 mixture. That is, one evaluation is from the third order rate expression while the other is from its derived pseudo-second order expression. That this numerical equivalence is more probably fortuitous is indicated by the inequalities obtained in the cases of the 3:1 and 1:1 mixtures.

Rolfe and Hinshelwood (1934) have shown that some single acetic acid molecules are necessary for catalysis. The fact that the rate expression given by equation 4 is not the best expression for any of the mixtures seems to substantiate their results and it indicates that any dimer formed in the chromatographic column does not alter the mechanism of the reaction.

Although equation 3 appears most applicable to the 3:1 and 1:1 mixtures, the precision of the k values is not good at the two higher temperatures. Furthermore, none of the k values agree with those obtained for the 1:3 mixture. However, the order of magnitude is consistent and in agreement with the determinations of k made by other methods. Further work is in progress in order to determine whether precisions within 10 per cent are possible in the determination of rate constants with the use of gas chromatography.

The kinetics of the esterification of *n*-propyl alcohol with acetic acid at temperatures between 70° and 80° have been studied by P'eng *at al.* (1938). They obtained a value of $k = 36.1 \times 10^{-4}$ liter-mole^{-1} hour^{-1} at 70° and $k = 64.2 \times 10^{-4}$ liter-mole^{-1} hour^{-1} at 80°. Both the magnitude of k and its change with temperature are consistent with the present study.

The energy calculated from Figure 5 is not a true activation energy but rather a composite energy. This is true even though the catalysis due to a proton and the catalysis due to a basic component have been neglected. Nevertheless, the energy cal-

culated by the present method may be compared with that calculated by P'eng *et al.* They obtained E= 13,550 cal/mole while the present calculation gives E=(16,000 ± 600) cal/mole. The higher result may be due in part to the lower operating temperature, but it may also be characteristic of gas chromatographic measurements. Correspondingly, the pre-exponential factor is smaller by a factor of 100 in the present work.

Summary

The specific reaction rates for the non-aqueous esterification of acetic acid and *n*-propyl alcohol were determined, using a gas chromatograph. The results are consistent with previous work on the same reaction. The method has proven useful in determining the rate constant near room temperature.

Acknowledgment

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