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Gas Chromatography. II. The Determination of Certain Physical Constants in the Alcoholysis of Esters

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Gas chromatography is shown to be ideally suited for the determination of equilibrium constants, rates of reactions and activation energies of organic reactions. This technique has been applied to the accurate determination of equilibrium constants for the alcoholysis of ethyl propionate, *n*-propyl propionate and ethyl *n*-butyrate with methanol and the alcoholysis of methyl propionate with ethanol and 1-propanol. The standard deviation for the equilibrium constant measurements was found to be within 1.2% of the mean value. The equilibrium constant for the simultaneous alcoholysis of methyl propionate and methyl *n*-butyrate mixture with ethanol, a six component system, has been measured and compared with a value calculated from individually measured equilibrium constants. The apparent rate constants and the activation energy for the methanolysis of *n*-propyl propionate in the presence of dry hydrogen chloride have been determined. The standard deviation for rate constant measurements was found to be less than 3% of the mean value. These reactions were chosen because the reaction mixtures, consisting of two alcohols, two or more esters, the catalyst, and minor amounts of alkyl halides present from side reactions are particularly difficult to analyze by other methods.

Gas chromatography has received widespread use in the determination of volatile organic materials. However, the applications of gas chromatography are not limited to strictly analytical purposes. In this paper the application of gas chromatography to the determination of equilibrium constants, reaction rates and activation energies of organic reactions is reported. In particular, the equilibrium constants for the alcoholysis of ethyl propionate, *n*-propyl propionate and ethyl *n*-butyrate with methanol, the alcoholysis of methyl propionate with ethanol and 1-propanol, and the simultaneous alcoholysis of methyl propionate and methyl *n*-butyrate mixture with ethanol in the presence of dry hydrogen chloride catalyst have been determined. The apparent rate constants and the activation energy for the methanolysis of *n*-propyl propionate in the presence of dry hydrogen chloride have been evaluated. The equilibrium constants, reaction rates and activation energies of these reactions have not previously been measured. These reactions were chosen because the reaction mixtures, consisting of two alcohols, two or more esters, the hydrogen chloride catalyst, and minor amounts of alkyl halides present from side reactions are particularly difficult to analyze by other methods.

Fehlandt and Adkins[2] have used fractional distillation as a separation technique in the study of the equilibrium mixtures formed by reaction of certain high molecular weight alcohols with methyl acetate. Farkas, *et al.*,[3] have studied the rate of butanolysis of ethyl acetate and Buess-Thiernagand and Fierens[4] the rate of methanolysis of *n*-butyl propionate and *n*-butyl acrylate using a technique which depends upon distribution of the two esters of the reaction mixture between the organic phase and an aqueous phase. Analysis of the total ester extracted into the aqueous phase was carried out by saponification, and empirical calibration curves were prepared from synthetic mixtures in the absence of catalyst. No discussion of the effect of the water used in the extraction on the reaction rate nor the effect of the catalyst concentration on the distribution coefficient of the esters was given.

The purpose of the work presented herein is not to determine a large body of fundamental physical data but rather to establish the precision of a method which will permit the evaluation of these data with greater ease and reliability than previously possible.

Experimental

Apparatus.—The chromatographic apparatus used was similar to that described by Bennett, *et al.*[5] Constant detector cell and column temperature was maintained by the vapor-jacket method described by Ray.[6] Reagent grade toluene was used as the reflux liquid to maintain the temperature at 110.6°.

A diaphragm-type, two-stage reducing valve (The Matheson Co.) connected in series with a Hoke needle valve and a 500-ml. brass buffer tank was found to give excellent control of column inlet pressure and flow rate. The helium flow rate, measured at 25° and one atmosphere pressure, was maintained constant at approximately 25 ml./min.

A pre-heater located between the buffer tank and the sample port was used to assure rapid vaporization of the liquid sample. The temperature of the pre-heated carrier gas was measured with a Conax thermocouple (Type AN-MTG-20-AS-21C, Conax Corporation, Buffalo, N.Y.) which was permanently mounted in the gas stream immediately before the sample inlet port. The heated gas stream was maintained at approximately 135°.

An "Agla" micrometer syringe (Burroughs Wellcome and Co., London) was used for sample injection. Correction was made, when required, for vaporization of the sample in the needle by the heated carrier gas. For samples containing hydrogen chloride this correction amounted to as much as 0.0013 ml. because of the extremely high vapor pressure of hydrogen chloride at the temperature of the heated carrier gas. Correction was made immediately after the needle was removed from the sample port by adjusting the syringe micrometer until the liquid sample appeared at the beveled tip of the needle. Reproducibility was better than 1%, and the corrected calibration curves were linear and passed through the origin. For samples not containing hydrogen chloride, the correction was of the order of 0.0003 ml., the exact value depending upon the volatility of the sample. Exact knowledge of sample size is *not* required for the accurate determination of equilibrium constants by gas chromatography. For the equilibrium studies the area under the curves was measured with an Keuffel and Esser Compensating Polar Planimeter. For the rate studies changes in component concentrations were followed by observing the changes in peak height (normalized to unit volume) with time.

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[1] Abstracted from a Dissertation submitted by F. M. Wachi to the Graduate School of the University of Illinois, 1959, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] P. R. Fehlandt and H. Adkins, THIS JOURNAL, **57**, 193 (1935).

[3] L. Farkas, O. Schlächter and B. H. Vromen, *ibid.*, **71**, 1991 (1949).

[4] D. Buess-Thiernagand and P. J. C. Fierens, *Bull. soc. chim. Belg.*, **61**, 403 (1952).

[5] C. E. Bennett, S. Dal Nogare, L. W. Safranski and C. D. Lewis, *Anal. Chem.*, **30**, 898 (1958).

[6] N. H. Ray, *J. Appl. Chem., London*, **4**, 21 (1954).

Several partition columns were required for complete separation of the various systems studied. The solid inert phase was either Johns-Manville C-22 firebrick (Sil-O-Cel) or Johns-Manville Celite 545. The C-22 firebrick was ground to 40/60 mesh, acid washed with hydrochloric acid to remove iron and basic impurities, washed thoroughly with water, and dried 4 hr. at 175°. The Celite was acid washed and size graded by the flotation method of James and Martin.[7]

The columns were approximately 9 feet long and were made from $^1/_4$-inch o.d. copper tubing shaped in the form of a W. The columns were divided into four sections designated A, B, C and D. The lengths of these sections were arbitrarily fixed at 44, 20, 18 and 26 inches, respectively. The composition of each section of several useful partition columns is given in Table I.

TABLE I

COMPOSITION OF THE PARTITION COLUMNS

Partition column no.	Weight % of liquid on inert support[a]			
	Section A (44 in.)	Section B (20 in.)	Section C (18 in.)	Section D (26 in.)
1	25% TCP[b]	40% Glycerol	25% TCP	35% Ether 181[c]
2	42% TCP	40% Glycerol	35% Ether 181	42% TCP
3	35% TCP	38% Ether 181[d]	35% Ether 181	35% TCP
4	33% TCP	25% Glycerol	35% Ether 181	33% TCP

[a] Johns-Manville C-22 Firebrick (40/60 mesh) used as solid support except where indicated. [b] Tri-*o*-cresyl phosphate (Pittsburgh Coke and Chemical Co.). [c] Tetraethylene glycol dimethyl ether (Ansul Chemical Co.). [d] Johns-Manville Celite 545 used as solid support.

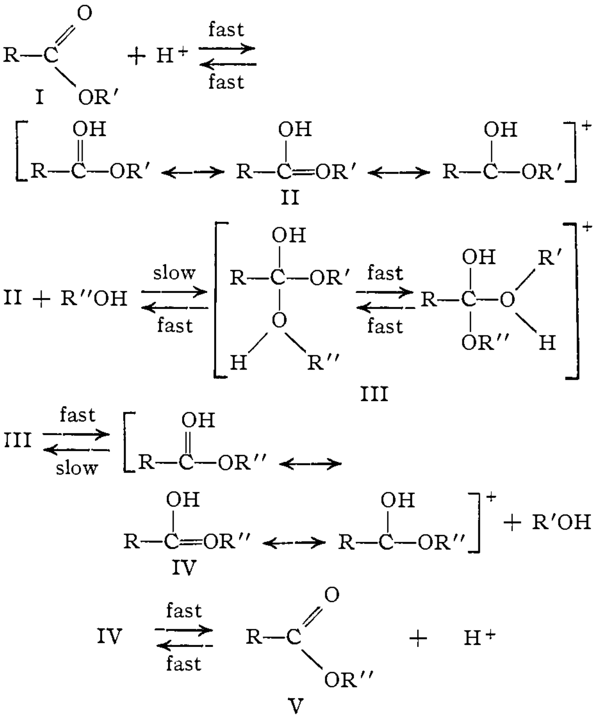
Rapid chromatographic separations were desirable in certain rate constant determinations. These were performed on a 4-ft. column which contained 8.6 g. of 35% by weight tri-*o*-cresyl phosphate on 30/50 mesh Sil-O-Cel and 7.3 g. of 30% by weight Carbowax 1000 on 30/50 mesh Sil-O-Cel.

Materials.—Eastman White Label grade esters were treated with anhydrous cupric sulfate[8] and distilled at atmospheric pressure under dry nitrogen. The alcohols, with the exception of ethanol, were dried with metallic magnesium in accordance with the method of Lund and Bjerrum.[9] Ethanol was dried with metallic sodium in the presence of ethyl phthalate[10] and then distillation under dry nitrogen. The water content of the purified solutions was determined by Karl Fischer titration and was found to be less than 0.05% by weight. All volatile reagents were tested for purity by gas chromatography and were shown to be "chromatographically pure." The limit of detection of the apparatus used in the present investigation was of the order of 10^{-8} mole.

Preparation of Samples.—The catalyst was prepared by absorbing dry hydrogen chloride[11] in the anhydrous alcohols. The hydrogen chloride content was determined acidimetrically, and the standardized solutions were used immediately in order to minimize loss of acid through volatilization and reaction with the alcohols. A calculated volume of acidified alcohol was added to either a 5-ml. oven-dried ampule (equilibrium studies) or a specially selected, tight-fitting, glass-stoppered 50-ml. flask (rate studies) under a dry nitrogen atmosphere. Great care was exercised in excluding moisture from the reactants during the sample preparation. The ester, which had been thermostated for at least 3 hr. at the temperature at which the rate of alcoholysis was being determined, was added rapidly from a pipet while the contents of the flask were being agitated by swirling. The flask was stoppered securely, shaken vigorously and immediately placed in the constant temperature bath. The time required to add the ester was less than 12 seconds. In the equilibrium studies the ampule was cooled to Dry Ice temperature before sealing the tip. The reaction mixtures then were equilibrated in constant temperature baths.

Theoretical

Day and Ingold[12] have suggested a mechanism for the acid hydrolysis of esters and have designated the reaction scheme, A'_2. Harfenist and Baltzly,[13] Farkas, *et al.*,[3] and Buess-Thiernagand and Fierens[4] have postulated somewhat analogous mechanisms for the alcoholysis of an ester.



The positive ion, II, a carbonium ion as advocated by Harfenist and Baltzly[13] or an oxonium complex as suggested by Farkas, *et al.*,[3] and by Buess-Thiernagand and Fierens,[4] reacts with the alcohol to form an addition complex, III, in a rate-controlling step. Thus the over-all rate-determining step becomes

$$\mathrm{II} + \mathrm{R''OH} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{IV} + \mathrm{R'OH}$$

where k_2 and k_{-2} are the second-order rate constants for the forward and reverse reactions. The rate expression describing the acid-catalyzed alcoholysis of I with R″OH has been shown by Farkas, *et al.*,[3] to be

$$k_2K_{\mathrm{II}}\,[\mathrm{H}^+]t = \frac{1}{\sqrt{q}} \ln \frac{2ab - x[(a+b) - \sqrt{q}]}{2ab - x[(a+b) + \sqrt{q}]} \quad (1)$$

where

$$q = (a+b)^2 - 4ab[1 - (1/K_{\mathrm{eq}})]$$

K_{II} is the formation constant of the positively charged intermediate, II; a and b are the initial concentrations of I and R″OH, respectively; and x is the concentration of V and R′OH at time $t > 0$.

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(7) A. T. James and A. J. P. Martin, *Biochem. J.*, **50**, 679 (1952).

(8) P. Salomaa, *Acta Chem. Scand.*, **11**, 125 (1957).

(9) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

(10) R. H. Manske, THIS JOURNAL, **53**, 1106 (1931).

(11) H. Taniguchi and G. J. Janz, *Anal. Chem.*, **28**, 287 (1956).

(12) J. N. E. Day and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 686 (1941).

(13) M. Harfenist and R. Baltzly, THIS JOURNAL, **69**, 362 (1947).

For the case where $a = b$, equation 1 reduces to $k_2' = k_2K_{\text{II}}[\text{H}^+] =$

$$\frac{1}{2at\sqrt{1/K_{\text{eq}}}}\ln\frac{a - x(1 - \sqrt{1/K_{\text{eq}}})}{a - x(1 + \sqrt{1/K_{\text{eq}}})} \quad (2)$$

where K_{eq} is the over-all equilibrium constant for the alcoholysis reaction. It may be seen that the second-order rate constant, k_2, cannot be determined unless the effective hydrogen ion concentration and the formation constant of the oxonium complex are known. Nevertheless, an apparent second-order rate constant, k_2', may be determined for any given catalyst concentration. Equation 2 also may be written

$$k_2' = \frac{x_{\text{e}}}{2at(a - x_{\text{e}})}\ln\frac{ax_{\text{e}} + x(a - 2x_{\text{e}})}{a(x_{\text{e}} - x)} \quad (3)$$

where x_{e} is x at $t = \infty$.

For the case where $b >> a$ (large excess of alcohol), the alcoholysis reaction may be considered as a pseudo-first-order forward reaction opposed by a second-order reaction. The apparent pseudo-first-order rate constant then is described by the equation

$$k_1' = k_1K_{\text{II}}b[\text{H}^+] = \frac{x_{\text{e}}}{(2a - x_{\text{e}})t}\ln\frac{ax_{\text{e}} + x(a - x_{\text{e}})}{a(x_{\text{e}} - x)} \quad (4)$$

Discussion and Results

Quenching the Reaction.—For most rate and equilibrium studies it is necessary to chemically quench the reaction before analysis, particularly if one or more components are removed from the reaction mixture. When gas chromatography is used in the separation and analysis of an alcoholysis reaction mixture and when hydrogen chloride is used as catalyst, it has been found that the catalyst is separated from the less volatile components on the chromatographic column at a rate rapid enough that no change in composition takes place and chemical quenching is not necessary.

Several observations suggested that hydrogen chloride was undergoing rapid volatilization and separation in the chromatographic column. (1) Hydrogen chloride was eluted far in advance of any other component in the reaction mixture, and its retention volume was very close to the gas hold-up of the column. (2) Vaporization of the sample in the needle during injection was much greater in the presence of hydrogen chloride (*ca.* 0.0013 ml.) than in the absence of hydrogen chloride (*ca.* 0.0003 ml.). This can only be explained by ejection of liquid from the needle by the rapid vaporization of hydrogen chloride at the temperature of the carrier gas. Hydrogen chloride may be assumed to be a relatively poor catalyst for the alcoholysis of esters in the vapor state since it is un-ionized and exists as the molecular species. Furthermore, the other components of the mixture also are separated rapidly on the column completely eliminating any possibility of further reaction. (3) The apparent equilibrium constants for the alcoholysis reactions investigated were not affected by the catalyst concentration. (4) The rate of alcoholysis showed the expected Arrhenius temperature dependence.

Therefore, when hydrogen chloride is used as a catalyst for these organic reactions, equilibrium and rate studies may be carried out by gas chromatography without prior chemical quenching of the catalyst.

Equilibrium Constants.—The equilibrium constant K^{A} for the methanolysis of ethyl *n*-butyrate was determined at 30.0° and is defined by the equation

$$K^{\text{A}} = \frac{(\text{EtOH})(\text{Me-}n\text{-But})}{(\text{MeOH})(\text{Et-}n\text{-But})}$$

where parentheses refer to molar concentrations rather than activities and EtOH, Me-*n*-But, MeOH and Et-*n*-But refer to ethanol, methyl *n*-butyrate, methanol and ethyl *n*-butyrate, respectively.

Two samples consisting of equimolar quantities of reactants, 35.1 mmoles of both ethyl *n*-butyrate and methanol, and 0.34 mmole (0.48 mole %) of dry hydrogen chloride catalyst were prepared and allowed to reach equilibrium. The minimum time required for the reaction mixture to attain equilibrium was determined by analyzing a sample every 4 hr. until a constant value for the equilibrium constant was obtained. The catalyst concentration was adjusted so that constant values were obtained after 30–40 hr. In many cases samples were allowed to stand more than one week before analysis was carried out.

TABLE II

EQUILIBRIUM CONSTANTS FOR THE ALCOHOLYSIS OF ESTERS AT 30.0°

System	Initial R''OH/RCOOR'	Mole % HCl	No. of detn.	Mean equilibrium constant and σ
MeOH + Et-*n*-But ⇄ EtOH + Me-*n*-But	1.00	0.48	2	$K^{\text{A}} = 1.54$
	3.36	.26	2	$K^{\text{A}} = 1.56$
			Mean	$K^{\text{A}} = 1.55 \pm 0.02$
MeOH + *n*-ProPro ⇄ *n*-PrOH + MePro	1.00	.50	2	$K^{\text{B}} = 1.74$
	2.00	.65	1	$K^{\text{B}} = 1.74$
n-PrOH + MePro ⇄ MeOH + *n*-ProPro	1.00	.90	3	$K^{\text{B}} = 1.74$
	1.00	.22	1	$K^{\text{B}} = 1.73$
			Mean	$K^{\text{B}} = 1.74 \pm 0.01$
MeOH + EtPro ⇄ EtOH + MePro	1.00	.49	7	$K^{\text{C}} = 1.70$
EtOH + MePro ⇄ MeOH + EtPro	1.00	.51	3	$K^{\text{C}} = 1.70$
	1.65	.92	1	$K^{\text{C}} = 1.68$
			Mean	$K^{\text{C}} = 1.70 \pm 0.02$

The components of the equilibrium mixture were separated on partition column No. 3 (Table I). A chromatogram of the mixture is shown in Fig. 1A. The presence of small quantities of methyl chloride and ethyl chloride formed from side reactions may be detected in the chromatogram. Small quantities of these products do not in any way affect the accuracy of equilibrium constants determined by gas chromatography. However, the formation of side products *would* influence the accuracy of any method in which the concentration of only one component of the equilibrium mixture was used to evaluate the equilibrium constant.

The effect upon the equilibrium constant of a 3.36-fold change in the initial mole ratio of reactants also was studied. Two samples were prepared consisting of 21.3 mmoles of ethyl *n*-butyrate, 71.6 mmoles of methanol and 0.24 mmole (0.26 mole %) of dry hydrogen chloride catalyst. The experimental results of all determinations are given in Table II. The apparent equilibrium constant K^A was found to be 1.55 ± 0.02 at 30.0°, independent of the initial mole ratio of reactants over the range in concentrations studied.

The equilibrium constant K^B for the methanolysis of *n*-propyl propionate was determined at 30.0° and is defined by the expression

$$K^B = \frac{(n\text{-PrOH})(\text{MePro})}{(n\text{-ProPro})(\text{MeOH})}$$

where *n*-PrOH, MePro and *n*-ProPro represent *n*-propanol, methyl propionate and *n*-propyl propionate, respectively.

Two samples were prepared so that each initially contained 30.4 mmoles of both *n*-propyl propionate and methanol and 0.30 mmole (0.50 mole %) dry hydrogen chloride catalyst. The components of the equilibrium mixture were separated on partition column no. 2 (Table I). The effect upon the apparent equilibrium constant of a twofold change in the initial methanol/*n*-propyl propionate ratio also was studied. The experimental results of these analyses are given in Table II. A mean value of 1.74 ± 0.02 was obtained for K^B at 30.0°, independent of the mole ratio of reactants.

The value of the equilibrium constant K^B was verified by measuring the equilibrium constant of the reverse reaction, *i.e.*, the propanolysis of methyl propionate. Three equimolar mixtures of 1-propanol and methyl propionate were prepared in the presence of 0.90 mole % hydrogen chloride. Another sample identical with the above, but containing only 0.22 mole % hydrogen chloride, also was prepared. The mean value of 1.74 ± 0.01 for K^B is in exact agreement with the value obtained by approaching equilibrium from the reverse direction.

The equilibrium constant K^C for the methanolysis of ethyl propionate was determined at 30.0° and is defined by the expression

$$K^C = \frac{(\text{EtOH})(\text{MePro})}{(\text{MeOH})(\text{EtPro})}$$

where EtPro represents ethyl propionate.

Seven identical samples containing 34.9 mmoles of both ethyl propionate and methanol and 0.34 mmole (0.49 mole %) of dry hydrogen chloride catalyst were prepared. Approximately 16 µl. of the equilibrium mixture was analyzed on partition column no. 1. The mean value of the equilibrium constant K^C at 30.0° is 1.70 ± 0.02.

The value of K^C was verified by running the reaction in the reverse direction, *i.e.*, the ethanolysis of methyl propionate. Two different initial reactants and catalyst concentrations were used. The mean value of K^C obtained was in exact agreement with that run in the opposite direction.

It is interesting to note that from the results reported by Buess-Thiernagand and Fierens[4] a value of 1.7 may be calculated for the equilibrium constant for the methanolysis of *n*-butyl propionate at 30.0°. Thus, the equilibrium constants for the methanolysis of ethyl propionate, *n*-propyl propionate and *n*-butyl propionate are practically independent of the alkoxy radical of the propionate esters.

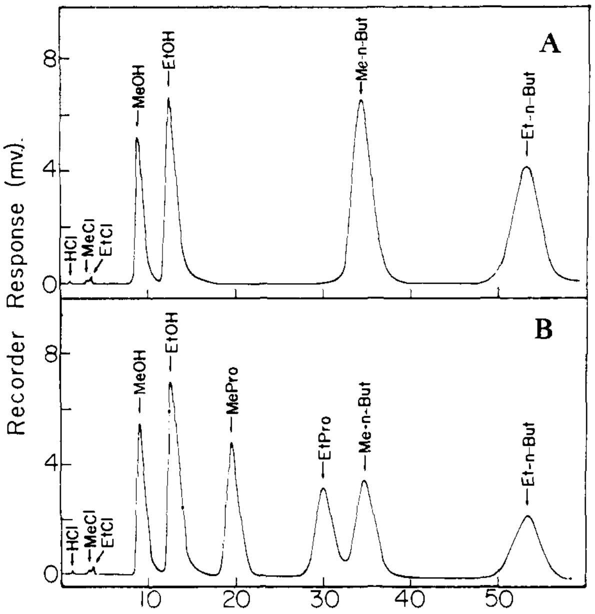

Fig. 1.—A. Gas chromatogram of the equilibrium mixture in the methanolysis of ethyl *n*-butyrate; B. chromatogram of a six component equilibrium mixture in the simultaneous ethanolysis of methyl propionate and methyl *n*-butyrate; column temperature, 110.6°; pre-heated helium temperature, 135°; flow rate, 23 ml./min.; partition column No. 3 (Table I).

The evaluation of the equilibrium constant for a six-component system was carried out by gas chromatography. This determination would be extremely difficult, if not impossible, by other analytical techniques. The simultaneous alcoholysis of methyl propionate and methyl *n*-butyrate with ethanol was chosen for the present investigation because the theoretical equilibrium constant may be calculated from the measured values of K^A and K^C. The apparent equilibrium constant for the reaction

$$\text{Me-}n\text{-But} + \text{MePro} + 2\text{EtOH} \underset{\text{HCl}}{\overset{K^{AC}}{\rightleftharpoons}} \text{Et-}n\text{-But} + \text{EtPro} + 2\text{MeOH} \qquad (5)$$

is given by the equation

$$K^{AC} = \frac{(\text{Et-}n\text{-But})(\text{EtPro})(\text{MeOH})^2}{(\text{Me-}n\text{-But})(\text{MePro})(\text{EtOH})^2}$$

K^{AC} is related to the individual equilibrium constants K^A and K^C by the expression

$$K^{AC} = 1/K^AK^C = 1/(1.55)(1.70) = 0.380$$

A sample containing 17.6 mmoles of both methyl *n*-butyrate and methyl propionate, 35.2 mmoles of ethanol and 0.48 mmole (0.68 mole %) of dry hydrogen chloride catalyst was prepared and allowed to reach equilibrium at 30.0°. Analyses of the equilibrium mixture were made on partition column No. 3. A chromatogram of the mixture is shown in Fig. 1B. The components were well resolved except for a slight overlap of ethyl propionate and methyl *n*-butyrate.

The mean value determined for K^{AC} was 0.399 ± 0.006, which may be compared with the value 0.380 calculated from K^{A} and K^{C}. The two values differ by only 5%. This agreement was considered remarkably good in view of the fact that a six component system was being studied and the component peaks were not all completely separated.

The effect of temperature upon the equilibrium constants, K^{B} and K^{C}, was studied. The purpose of this investigation was to determine whether free energies, the entropies and the heats of reaction for the alcoholysis of esters could be evaluated from measurements of changes in the apparent equilibrium constants with temperature.

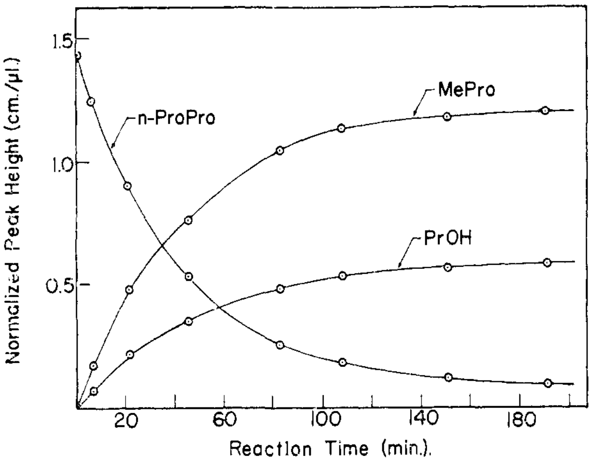

Fig. 2.—Rate study: the alcoholysis at 30.0° of *n*-propyl propionate with a 12-fold excess of methanol. The variation of normalized peak heights (concentrations) of the products and the reactant with time.

Four determinations of the value of K^{C} were made at 0.0 ± 0.1° using initial concentrations of methanol to ethyl propionate of 1:1. The mean value and standard deviation was $K^{C} = 1.71 \pm 0.01$ at 0.0°, within experimental error of the value found at 30.0°. Two determinations of the value of K^{B}, the methanolysis of *n*-propyl propionate, were made at 20.0°. The mean value obtained was 1.73, again within experimental error of the value found at 30.0°. Thus, the equilibrium constants are essentially independent of the temperature between 0 and 30°. A similar observation has been recorded by Farkas, *et al.*[3] They have reported an equilibrium constant of 0.96 for the alcoholysis of ethyl acetate with 1-butanol in the temperature range 60 to 80° and have pointed out that this value is in good agreement with the value 0.97 obtained at 200° from the data of Fehlandt and Adkins.[2] Since the equilibrium constant is essentially independent of the temperature, it may be concluded that the Arrhenius activation energies for the forward and reverse reactions are nearly the same.

Rate Studies.—The apparent pseudo-first-order rate constant for the alcoholysis of *n*-propyl propionate with a large excess of methanol was determined at 20 and 30°. A rate experiment for a mixture containing a 12-fold excess of methanol is shown in Fig. 2. Since the volume of sample is not conveniently reproducible in each successive analysis by the syringe technique in the presence of hydrogen chloride, the peak heights were normalized to unit volume of sample in the kinetic studies. In principle, the apparent rate of alcoholysis may be calculated from changes in concentration of all components with time thus affording several independent checks on the rate from one single rate experiment, a distinct advantage of gas chromatography over most other methods. However, in the present investigation because of the large excess of methanol used in the pseudo-first-order experiments the three peaks of 1-propanol, methyl propionate and methanol were not sufficiently resolved for the most precise measurements. Therefore the change in concentration of *n*-propyl propionate alone was used to obtain the apparent rate of alcoholysis.

Mole ratios of methanol/*n*-propyl propionate greater than *ca.* 15:1 are not conveniently run with thermal conductivity detectors because the chromatographic column must then be flooded with the alcoholysis mixture before a sufficiently large peak is obtained for *n*-propyl propionate. Flooding the column causes the column characteristics to change rapidly. Precise analysis is then rather difficult. More sensitive detector systems would be of value in extending this range.

The alcoholysis of *n*-propyl propionate with a 15-fold excess of methanol in the presence of 1.28 mole % hydrogen chloride was studied at 20 and 30° using partition column no. 4 (Table I) to separate the components of the mixture. Approximately ten chromatograms were taken during the course of the reaction. Since 65 minutes were required to elute the *n*-propyl propionate peak with column No. 4, four or five samples identical in composition were prepared in order to provide a sufficient number of points. The apparent pseudo-first-order rate constant was calculated for each point by equation 4. The results are given in lines 1 and 2, Table III. The activation energy calculated from these results is 12.8 kcal./mole. It is of interest to note that the value 12.7 kcal./mole was obtained by Buess-Thiernagand and Fierens[4] for the methanolysis of *n*-butyl propionate.

The effect of hydrogen chloride concentration upon the observed rate of alcoholysis of *n*-propyl propionate with methanol was studied at 30.0°. Experiments were performed at an initial methanol to *n*-propyl propionate mole ratio of 12:1 and catalyst concentrations of 0.99 and 2.52 mole % hydrogen chloride. The experimental results are given in lines 3 and 4 of Table III. The rate of alcoholysis increased by a factor of 2.6 for a 2.5-fold change in catalyst concentration.

The results of a similar experiment for an initial methanol/*n*-propyl propionate ratio of 8:1 is given in lines 5 and 6 of Table III. The rate of alcoholysis increased by a factor of 2.9 for a 3.2-fold change in catalyst concentration. These results indicate that the apparent rate of alcoholysis is essentially directly proportional to the catalyst concentration.

The apparent second-order rate constants for the

TABLE III

RATE OF METHANOLYSIS OF *n*-PROPYL PROPIONATE

Initial mmoles of reactants					
MeOH	*n*-ProPro	MeOH/*n*-ProPro	Mole % HCl	Temp., °C.	Mean rate constant × 10^4 and σ^a
909	60.8	15:1	1.28	20.0	$k_1' = 2.18 \pm 0.08$
902	60.2	15:1	1.27	30.0	$k_1' = 4.5 \pm .3$
906	75.2	12:1	0.99	30.0	$k_1' = 3.7 \pm .1$
906	75.2	12:1	2.52	30.0	$k_1' = 9.6 \pm .1$
903	113	8:1	0.82	30.0	$k_1' = 3.1 \pm .2$
903	113	8:1	2.67	30.0	$k_1' = 9.0 \pm .1$
246	245	1:1	4.28	20.0	$k_2' = 0.32 \pm .01^b$
245	245	1:1	4.19	25.0	$k_2' = .41 \pm .01^b$
244	244	1:1	4.20	30.0	$k_2' = .60 \pm .01^b$

[a] Units of pseudo-first-order kinetics, sec.$^{-1}$; second-order kinetics, l. mole^{-1} sec.$^{-1}$. [b] Mean value for the first 40% of reaction only.

methanolysis of *n*-propyl propionate were determined at 20.0, 25.0 and 30.0°. Each sample was analyzed at intervals of approximately 17 min. by gas chromatography with the rapid 4-ft. TCP-Carbowax column. The apparent second-order rate constants were calculated for each point along the decay curve by equation 3. The calculated rate constants were found to decrease by as much as 12% as the reaction approached equilibrium. This decrease in the apparent rate of alcoholysis may be caused by: (1) the change in solution composition during reaction; (2) the reduction in the concentration of the hydrogen chloride catalyst by side reactions (the halogenation of the alcohols as well as the formation of hydronium ion from the water formed in the halogenation reaction) which proceed at a significant rate at the catalyst concentrations used in these experiments. Nevertheless, essentially constant values were obtained for the rate constant during the first 40% of the reaction. The apparent second-order rate constants for the first 40% of the reaction were found to be (3.2 ± 0.1) × 10^{-5}, (4.1 ± 0.1) × 10^{-5}, and (6.0 ± 0.1) × 10^{-5} l. mole^{-1} sec.$^{-1}$ at a catalyst concentration of *ca.* 4.2 mole % hydrogen chloride (see Table III) and temperatures of 20.0, 25.0 and 30.0.°, respectively.

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URBANA, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF KANSAS]

The Dissociation Energy of Fluorine and the Magnetic Deflection of its Molecular Beams[1,2]

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A molecular beam of fluorine atoms and molecules issuing from a furnace passed through an inhomogeneous magnetic field and impinged on a detector of thin tellurium metal. It was shown that the detector responded to atoms alone. Two kinds of measurements of the atomic beam were made. They were absolute intensity measurements at two different temperatures and relative intensity measurements at several different temperatures. Dissociation energies obtained from the two kinds of measurements are in good agreement, and the average of six determinations by the second method is D_0 = 41.3 ± 0.5 kcal./mole.

Previous work with fluorine has not established an entirely certain value for its dissociation energy. Some estimates and measurements, mostly early ones, led to values of about 60 kcal./mole,[3] or higher while others of a more direct nature strongly favor a value in the range 35 to 40 kcal./mole.[4]

The fractional dissociation of fluorine, α, is a sensitive function of the dissociation energy D_0. Doescher,[4g] Gilles and Margrave,[4h] and Wise[4k] attempted to establish α and hence D_0 by measuring some property of fluorine, such as a pressure or rate of effusion. They assumed that the difference between the measured and expected values was caused by the presence of atoms in the equilibrium gas. Their results indicate a low value but have been criticized[3j] because of possible errors arising from impurities and corrosion of the furnace.

The present work is an attempt to establish α and D_0, but it involves a unique feature designed to

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(2) Taken in part from the Ph.D. thesis of Thomas A. Milne, University of Kansas, 1954.

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