CATALYSIS AND EQUILIBRIUM IN ACIDOLYSIS OF ESTERS

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PREFACE

A recent article by Juvet and Wachi (26) described the use of gas chromatography to determine some equilibrium and rate constants in alcoholysis of esters. The acidolysis or acid exchange of esters has long been known; however, little has been done to determine relative effectiveness of various catalysts or to determine how electronic or steric factors influence the equilibrium between a pair of acids and their esters. Our intention was to develop a gas chromatographic technique to study this reaction and to determine the effectiveness of various catalysts and the effect of electronic and steric factors on the equilibrium constant.

The author wishes to express his sincere appreciation for advice and counsel by Dr. O. C. Dermer under whose direction this work was done. He would also like to acknowledge the support and encouragement of the Management and co-workers of Continental Oil Company and expecially Doctors M. T. Atwood and F. Kennedy.

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INTRODUCTION

In a reversible homogeneous reaction such as

$$A + B \rightleftharpoons C + D$$

the rate of the direct reaction from left to right is kC_AC_B, assuming the concentrations by the C terms to give a measure of the active masses. The rate of the reverse reaction is $k'C_CC_D$. At equilibrium the rates of the two reactions are equal, so that

$$kC_AC_B = k'C_CC_D$$

$$\therefore \frac{C_CC_D}{C_AC_B} = \frac{k}{k'} = K_e$$

where K_e is defined as the equilibrium constant of the reaction.

Equilibrium constants have been determined for many organic reactions. In particular, the esterification of organic acids with alcohols has been studied in great detail; however, the products of this reaction are such that the resulting solution is not ideal. Consequently, in esterification the equilibrium constant is not independent of catalyst concentration. For example, Trimble and Richardson (39) found a straight line relation between equilibrium constant and concentration of catalyst. For acetic acid-ethanol esterification catalyzed with perchloric acid the equilibrium constant was 4.05 with 1N perchloric acid and 10.60 with 4N perchloric acid. Nor is the point of equilibrium always independent of concentration of reactants. Carso and Durruty (36) found large variations in the equilibrium constant as the ratio of acetic acid to ethanol was changed.

Another organic reaction for which equilibrium constants have been determined is the alcoholysis of esters. That is

$$\text{Ester I} + \text{Alcohol I} \rightleftharpoons \text{Ester II} + \text{Alcohol II} \; .$$

The rate of this exchange is greatly increased by an acid catalyst. This reaction has been recently studied by Juvet and Wachi (26) and some equilibrium constants and rate constants determined by gas chromatography. In this study it was shown that the equilibrium constant is independent of catalyst concentration within the range of 0.22 to 0.90 mole percent. The equilibrium constant was also shown to be independent of initial concentration of reactants over a threefold range.

In the case of either hydrolysis of esters or esterification, the products are considerably different from the reactants.

$$RCOOR' + H_2O \rightleftharpoons RCOOH + R'OH$$

At equilibrium the reaction product consists of a mixture of ester, water, acid and alcohol. The equilibrium constant for this reaction is

$$K_{\text{hydro.}} = \frac{[RCOOH]\,[R'OH]}{[RCOOR']\,[H_2O]} \; .$$

The values in the above equation in practice are usually molar concentrations rather than activities. With four different chemical types involved a deviation from "ideal" should be expected.

In acidolysis of esters, as in alcoholysis, only two chemical types are involved. Thus,

$$\text{Ester I} + \text{Acid I} \rightleftharpoons \text{Ester II} + \text{Acid II}$$

$$K_{\text{acidolysis}} = \frac{[\text{Ester II}]\,[\text{Acid II}]}{[\text{Ester I}]\,[\text{Acid I}]}$$

At least for small differences in the structure of Ester I and Ester II and in Acid I and Acid II, one should expect little deviation in the equilibrium constant as initial concentrations or catalyst concentrations are changed. Thus, we expected the system to be nearly ideal and follow the law of mass action. Therefore, a reliable comparison should be obtained between different catalysts. Variations in electronic and steric factors should be meaningful.

The first quantitative study of acidolysis of esters was made by Reid (34). In this study the equilibrium constants for the uncatalyzed reaction of benzoic acid with benzyl acetate and p-bromobenzoic acid with ethyl benzoate, each at about 210°, were determined by density measurements on the equilibrated system. The equilibrium constants appeared to be about 1.

Sudborough and Karve (37) reported in a paper, of which only an abstract has been used, an equilibrium constant of unity for acidolysis in the reactions of trichloroacetic acid with methyl acetate and trichloroacetic acid with ethyl acetate.

Gault and Chablay (14) studied the reaction of acetic acid with methyl palmitate and reported only 9.07 percent methyl acetate to be produced in 500 hours at 100°; however, methyl acetate and palmitic acid reached equilibrium after 1000 hours. By using 5 percent sulfuric acid in the first reaction and 0.5 percent sulfuric acid in the second reaction, equilibrium was reached in fifty and twelve hours, respectively. At 100° the equilibrium constant for the reaction of methyl acetate and palmitic acid was 1.070.

In a later paper this work was extended by Gault and Chablay (15) to other acids. These experiments were run uncatalyzed in a sealed tube at 175°. Approximately thirty days were required to reach equilibrium. The equilibrium constant was reported to be independent of temperature and independent of concentration of reactants.

In a later study Chablay (7) extended this work to include heptanoic and octanoic acid. The entire series of equilibrium constants determined by Gault and Chablay (14,15,7) is presented in Table I.

TABLE I

EQUILIBRIUM CONSTANTS FOR ACIDOLYSIS
OF METHYL PALMITATE[‡]

Acid	K_e
Acetic	1.074
Propanoic	1.040
Butanoic	1.096
Pentanoic	1.024
Hexanoic	0.997
Heptanoic	1.05
Octanoic	1.01

[‡] These equilibrium constants were determined at 175° without catalyst.

Sowa (36) studied the exchange of acetic acid with various alkyl esters of propionic, benzoic and salicylic acid at 100°. The catalysts used were sulfuric acid, zinc chloride, boron trifluoride and dihydroxyfluoboric acid. After one hour the extent of exchange of acetic acid with n-butyl propionate in the presence of these catalysts were 21, 31, 40, and 60 percent, respectively. No claim of attainment of equilibrium was made. Analysis of the product was by distillation of the ester after a water extraction of the organic acid. An interesting feature of this work was that the reaction of n-butyl propionate and acetic acid catalyzed by boron trifluoride was said to produce butyl acetate which was ten percent rearranged to s-butyl acetate. In the reaction of isobutyl propionate and acetic acid the product ester was said to be 30 percent rearranged. No mention was made in the paper as to how this extent of rearrangement was determined.

Barkenbus and coworkers (4) made a large-scale run using n-butyl stearate and acetic acid to see if this alkyl rearrangement occurred for esters of higher fatty acids. The n-butyl acetate was separated and fractionated through a ten-plate Podbielniak column. Only two percent of the ester had rearranged to s-butyl acetate.

In the work of Barkenbus the acidolysis equilibrium was approached from one direction only. Their procedure involved heating either the acetic or formic ester with stearic acid to 100° in the presence of two weight percent p-toluenesulfonic acid. The equilibrated mixture was water-extracted to separate the acetic or formic acid from stearic acid. Most consistent results were obtained by titration of the water-insoluble acid. Very good agreement was obtained when the Barkenbus results were compared with the Gault and Chablay (14,15,7) results. The Barkenbus equilibrium constants are in Table II, excepting that for methyl acetate and palmitic acid, which was 1.034.

TABLE II

EQUILIBRIUM CONSTANTS FOR ACIDOLYSIS OF ESTERS WITH STEARIC ACID[#]

Ester	Formates	Acetate
Methyl	1.287	1.019
Ethyl	0.845	0.902
n-Propyl	0.794	0.912
s-Propyl	0.693	-
n-Butyl	0.869	0.964
i-Butyl	0.782	-
n-Amyl	0.750	-

[#] These equilibrium constants were at 100° with p-toluenesulfonic acid-hydrate catalyst.

Korshak and Vinogradova (28) reported in a Russian paper, of which only an abstract has been used, measurement of the extent of uncatalyzed reaction of ethyl stearate and acetic acid at 123°, 168°, 183° and 250°. When equilibrium constants are calculated from the data reported a value of only one-tenth the value found by Barkenbus (4) and by Gault and Chablay (14) is obtained. The explanation for this is the short reaction time used by the Russian which did not permit attainment of equilibrium.

Recently the acidolysis reaction has been used to prepare certain esters. For example, bivinyl adipate was prepared from vinyl acetate and adipic acid using dry HCl as catalyst (13). Enjay Corporation disclosed in a technical bulletin that vinyl neopentanoate can be prepared by combining vinyl acetate with neopentanoic acid in the presence of mercuric sulfate catalyst (12).

Kenyon and coworkers (3) described the uncatalyzed reactions of the optically active hydrogen phthalate and benzoate of dimethylallyl alcohol with formic acid and with acetic acid. It was demonstrated that when the alkyl group has electron-releasing properties alkyl-oxygen fission occurs. Their work was based on measurements of optical activity.

EXPERIMENTAL

Apparatus

The chromatograph was an AEROGRAPH model A-350-B manufactured by Wilkins Instrument and Research, Incorporated. This was a dual-control automatic linear-temperature-programming thermal-conductivity instrument. A multi-speed HONEYWELL Electronik 15 strip chart chromatograph recorder was used. The recorder had a range of -0.05 to +1.05 millivolts. A chart speed of two inches per minute was used at all times.

The instrument injection port temperature was 270°. The detector cell temperature was 260°. Column temperature was initially 100° and programmed for a 10° rise per minute. A helium carrier gas was used at 80 p.s.i.g. with a flow rate of 80 ml. per minute through each column.

A one-microliter injection was used in the major portion of this work. After an instrument refinement which reduced electrical noise and improved base-line stability, it was possible to use a 0.5-microliter sample. Greater resolution was then obtained.

The instrument columns were ten-foot by 3/8-inch aluminum tubing. The columns were packed with 25 percent diethylene glycol succinate and 2 percent phosphoric acid on either firebrick or Celite as described by Metcalf (30). Excellent acid separation and good peak shape were obtained on acids of molecular weight from acetic to hexanoic. Formic acid tailed badly on these columns and could not be used. Cyclohexanecarboxylic acid and chloroacetic acid peak shapes were broad and less satisfactory.

Diethylene glycol succinate-phosphoric acid columns were remarkably stable up to 200°. One set of columns was used for over two years. A malfunctioning temperature controller caused overheating and loss of these columns.

Of the two different packing materials used, firebrick appeared to be best. Ester resolution was better than on Celite packing.

Component concentrations were obtained from peak area calculations. The peak area was determined by a triangulation technique which consisted of multiplying peak height by peak band width at one-half the peak height. By using a magnifying glass and a ruler with 100 divisions per inch the average peak height could be determined with a reproducibility of ±0.2 percent. The half-band widths were measured with a Bausch and Lomb measuring magnifier with 200 divisions per inch. The lowest molecular weight esters gave the narrowest peaks. These could be measured with a reproducibility of ±0.5 percent.

The peak area was converted to weight percent by determining an area correction factor for each component in each combination in which they were used. These area correction factors were always determined within a few days of the time they were needed. Changes in column absorption characteristics were thereby minimized.

Instrument resistor errors were minimized by using the same instrument settings on the standards as on the unknowns.

In Table III are listed the esters and acids used in this work. The component retention time is given in minutes. This may vary slightly owing to slight differences in temperature programming and slight differences in carrier gas flow. Where more than one area correction factor is given the factor was determined in different combinations of acids and esters.

TABLE III

G.C. RETENTION TIMES AND AREA CORRECTION FACTORS

Component	Retention Time, Minutes	Area Correction Factor
Methyl Acetate	1.4	0.76-1.00
Methyl Propanoate	1.9	1.02
Methyl Butanoate	2.2	1.02
Methyl 2-Methylpropanoate	1.7	1.02
Methyl Pentanoate	3.1	0.99
Methyl 3-Methylbutanoate	2.3	1.02
Methyl Hexanoate	4.0	0.98
Methyl 3,3-Dimethylbutanoate	2.3	1.03
Methyl Cyclohexanecarboxylate	6.8	1.04
Methyl Acrylate	1.9	1.00
Methyl Methoxyacetate	5.3	0.97
Methyl Chloroacetate	5.8	0.87
Ethyl Acetate	1.6	0.99
Ethyl Propanoate	2.0	1.01
Propyl Acetate	2.1	1.01-0.99
Propyl Propanoate	2.5	-
Methylethyl Acetate	1.6	1.01
Methylethyl Propanoate	1.9	1.02
Butyl Acetate	3.1	0.99-1.00
Butyl Propanoate	3.6	0.99-1.01
2-Methylpropyl Acetate	2.2	1.04
2-Methylpropyl Propanoate	2.7	1.01
1-Methylpropyl Acetate	2.1	1.02
1-Methylpropyl Propanoate	2.5	1.02
Acetic Acid	7.2	0.94-0.98
Propanoic Acid	8.1	0.97-1.02

III (Continued)

Component	Retention Time Minutes	Area Correction Factor
Butanoic Acid	9.0	1.03
2-Methylpropanoic Acid	8.5	1.05
Pentanoic Acid	10.7	1.07
3-Methylbutanoic Acid	9.5	1.05
Hexanoic Acid	11.9	1.08
3,3-Dimethylbutanoic Acid	9.6	1.10
Cyclohexanecarboxylic Acid	19.5	1.11
Acrylic Acid	9.3	1.11
Methoxyacetic Acid	16.0	1.30
Chloroacetic Acid	23.0	2.55

A constant temperature oil bath was used for the equilibrium study. It was maintained at 45 ±0.1°. The temperature controller was a THERMO-O-WATCH electronic controller, model number L-4, manufactured by Instruments for Research and Industry. It was attached to a mercury thermometer of 0.1° graduation. The oil bath was circulated with an air-driven stirring motor. Eighteen samples could be accommodated at one time.

Chemicals

Organic Acids:

Acetic acid - Reagent grade with no impurities by G.C. analysis.

Propanoic acid - As per acetic acid.

Butanoic acid - As per acetic acid.

2-Methylpropanoic acid - As per acetic acid.

Pentanoic acid - As per acetic acid.

3-Methylbutanoic acid - Reagent grade redistilled. A thirty percent heart cut was taken with b.p. 176°. The final product was 98.3 percent pure by G.C. analysis.

Hexanoic acid - As per acetic acid.

3,3-Dimethylbutanoic acid - Custom-made by Frinton Laboratories, South Vineland, New Jersey, and redistilled. A forty percent heart cut was taken with a b.p. of 183-184°. The final product was 96.5% pure by G.C. analysis.

Cyclohexanecarboxylic acid - As per acetic acid.

Acrylic acid - As per acetic acid except for p-methoxyphenol inhibitor.

Methoxyacetic acid - As per acetic acid.

Chloroacetic acid - As per acetic acid.

Esters:

Methyl acetate - Reagent grade with no impurities by G.C. Dried over Linde 3A molecular sieves.

Methyl propanoate - As per methyl acetate.

Methyl butanoate - As per methyl acetate.

Methyl 2-methylpropanoate - As per methyl acetate.

Methyl pentanoate - Prepared from methanol and pentanoic acid by the esterification technique of Harrison, Haynes, Arthur and Eisenbraun (19). Excess methanol was refluxed through 3A molecular sieves to adsorb water. Heart-cut ester distilled at 126°. It contained no impurities by G.C.

Methyl 3-methylbutanoate - Prepared from methanol and isovaleryl chloride in the presence of N,N-dimethylaniline by the method of Abramovitch, Shivers, Hudson and Hauser (1). Heart-cut ester distilled at 116°. It was 99.2 percent by G.C.

Methyl hexanoate - Technical grade purified by preparative G.C. on an Apiezon L column. The product contained no impurities by G.C.

Methyl 3,3-dimethylbutanoate - As per 3,3-dimethylbutanoic acid. A forty percent heart cut, b.p. 126-127°, was taken. It was 99.8% pure by G.C.

Methyl cyclohexanecarboxylate - As per methyl pentanoate. Heart-cut ester distilled at 74-75° at 18 mm. There were no impurities by G.C.

Methyl acrylate - As per acrylic acid.

Methyl methoxyacetate - As per methyl pentanoate. Heart-cut ester distilled at 126-128.5°. It was 99.7 percent pure by G.C.

Methyl chloroacetate - As per methyl acetate.

Ethyl acetate - As per methyl acetate.

Ethyl propanoate - As per methyl acetate.

Propyl acetate - As per methyl hexanoate.

Propyl propanoate - As per methyl acetate.

Methylethyl acetate - As per methyl acetate.

Methylethyl propanoate - As per methyl acetate.

Butyl acetate - As per methyl acetate.

Butyl propanoate - As per methyl acetate.

2-Methylpropyl acetate - As per methyl acetate.

2-Methylpropyl propanoate - As per methyl acetate.

1-Methylpropyl acetate - As per methyl hexanoate.

1-Methylpropyl propanoate - As per methyl 3-methylbutanoate. Heart-cut ester distilled at 126-128°. It was further purified by preparative G.C. The product contained no impurities by G.C.

1,1-Dimethylethyl acetate - As per methyl hexanoate.

1,1-Dimethylethyl propanoate - As per methyl 3-methylbutanoate. Heart-cut ester distilled at 116-117°. It contained 1 percent impurities by G.C. Purification by preparative G.C. produced a pure product.

Miscellaneous Chemicals and Reagents:

Acetic anhydride - Reagent grade.

Aluminum chloride - Reagent grade.

Boron trifluoride-ethyl etherate - Reagent grade.

sec.-Butyl alcohol - Reagent grade.

tert.-Butyl alcohol - Reagent grade.

Calcium acetate - Reagent grade dried in vacuum oven at 130° overnight.

_N_,_N_-Dimethylaniline - Redistilled reagent grade.

Ethanol - Absolute, dried over Linde 3A molecular sieves.

Hydrochloric acid - Reagent grade.

Hydrogen chloride - Reagent grade anhydrous.

Isovaleryl chloride - Reagent grade.

Mercuric sulfate - As per calcium acetate.

Methanol - Absolute.

Molecular sieves - Linde 3A for drying esters and ethanol. Linde AW-500 for drying acetic acid containing one mole percent $HClO_4$ and two mole percent H_2O.

Perchloric acid - Reagent grade - 70 percent $HClO_4$ in water.

Propionyl chloride - Two different batches were used. One was reagent grade redistilled. The other was prepared from thionyl chloride and propanoic acid and distilled.

Pyridine - Reagent grade.

Sodium acetate - As per calcium acetate.

Sodium chloride - As per calcium acetate.

Sodium sulfate - As per calcium acetate.

Sulfuric acid - Reagent grade.

para-Toluenesulfonic acid monohydrate - Reagent grade, ALFA Inorganic, Beverly, Massachusetts.

Zinc chloride - As per calcium acetate.

General Procedure

Determination of the equilibrium constant for the reaction

$$\text{Ester I} + \text{Acid I} \rightleftharpoons \text{Ester II} + \text{Acid II}$$

began with weighing into a plastic-lined screw-cap one-ounce bottle 0.01 mole of Ester I and 0.01 mole of Acid I containing 1 mole percent catalyst. Two identical samples were prepared.

Two comparable samples were prepared starting with Ester II and Acid II containing a like quantity of catalyst. The samples were mixed thoroughly and submerged in the constant temperature bath at 45.0 ±0.1°. An attempt was made to allow sufficient time for attainment of equilibrium before the samples were removed from the bath.

Just prior to the analyses of the first samples a G.C. standard was prepared. This sample was a mixture of 0.01 mole each of Ester I, Ester II, Acid I and Acid II. The components were weighed to the nearest 0.1 milligram, so that weights were known to an accuracy of greater than 0.1 percent. The G.C. standard was analyzed three or four times under operating conditions as nearly as possible identical to conditions used for equilibrium samples. An average area correction was determined for each component of the combination.

Multiplying observed area by correction factor made the corrected area percent equal to weight percent. G.C. standards could be duplicated with a reproducibility of ±1 percent.

After the samples were removed from the constant temperature bath they were immediately cooled in ice water. They were analyzed on the G.C. unit and restoppered. The values for equilibrium constants were calculated from the equation

$$K_e = \frac{[\text{Ester II}]\,[\text{Acid II}]}{[\text{Ester I}]\,[\text{Acid I}]}$$

where the values in brackets are mole fractions. The equilibrium constant determined for the reaction

$$\text{Ester I} + \text{Acid I} \rightleftharpoons \text{Ester II} + \text{Acid II}$$

proceeding from left to right is, of course, the reciprocal of the equilibrium constant for the reaction proceeding from right to left.

If the reaction from left to right did not yield the same value for K_e as the reaction from right to left, the samples were returned to the constant temperature bath for an additional reaction period.

Acceptance of a value as most probable for the equilibrium constant required good agreement of at least three of the four values. If the deviation of one of the four values was greater than the average deviation of three similar values it was rejected in calculating the average. Several times during the course of this work a sample giving deviant results was placed back into the constant temperature bath for an additional reaction period. In every case the new value agreed with the average of the accepted three samples.

Removal of Water From Acetic Acid

Acetic acid containing one mole percent perchloric acid was prepared from a 70 percent perchloric acid-water solution. It was analyzed for water by the Karl Fisher technique (23) and found to contain 0.94 weight percent water. Acetic anhydride in 10 percent excess of the stoichiometric requirement was added to consume the water. After two days the acetic acid was again analyzed. The water content was 0.0070 weight percent.

A second acetic acid-perchloric acid solution was prepared in the same manner and dried over Linde AW-500 molecular sieves. It was not analyzed for water.

A third acetic acid-perchloric acid solution was prepared. It was dried with acetic anhydride and analyzed. It contained 0.0015 weight percent water.

RESULTS AND DISCUSSION

Results of Equilibrium Constant Determinations

For illustration consider the acidolysis of methyl acetate with propanoic acid. Table IV presents the area percent correction factor for converting area percent to weight percent. Table V is an example of one determination of equilibrium constant. In this table the mole fractions of ester and acid charge are given, and then the mole fractions of the components at equilibrium.

Tables VI through XXII are summaries of the equilibrium constants determined in this study. In each case, as shown, these equilibrium constants were determined on two samples approaching equilibrium from the left and two samples approaching from the right. For simplicity and uniformity, K_e values presented are either those obtained approaching from the left or the reciprocals of those approaching from the right.

The quantity of catalyst in each equilibrium experiment was expressed as mole percent based on organic acid charged.

Effect of Water or Alcohol in Acidolysis of Esters

To evaluate the importance of water in the acidolysis of esters, an anhydrous system was devised. This was done by drying a one mole percent solution of perchloric acid in acetic acid as

TABLE IV

G.C. AREA CORRECTION FACTOR

Sample	Component	Weight Percent	Calculated Area Percent 1	2	3
1	Methyl Acetate	23.9	24.2	24.1	-
	Methyl Propanoate	23.9	23.3	23.4	-
	Acetic Acid	27.4	28.1	27.8	-
	Propanoic Acid	24.8	24.4	24.7	-
2	Methyl Acetate	31.6	31.9	31.1	30.8
	Methyl Propanoate	20.8	20.4	20.4	20.4
	Acetic Acid	25.1	25.1	25.6	26.3
	Propanoic Acid	22.5	22.6	22.9	22.6

Sample	G.C. Area Correction Factor, Wt. Percent/Area Percent Methyl Acetate	Methyl Propanoate	Acetic Acid	Propanoic Acid
1-1	0.99	1.02	0.98	1.02
1-2	0.99	1.03	0.98	1.00
2-1	0.99	1.02	1.00	1.00
2-2	1.02	1.02	0.98	0.98
2-3	1.02	1.02	0.95	1.00
Average	1.00	1.02	0.98	1.00
Average Deviation	0.014	0.002	0.010	0.008

TABLE V

EQUILIBRIUM: METHYL ACETATE AND PROPANOIC ACID[‡]

		Mole Fraction				
Sample		Methyl Acetate	Propanoic Acid	Methyl Propanoate	Acetic Acid	K_e
2-75-1	Charge	0.500	0.500	-	-	
	Product	0.344	0.337	0.335	0.333	0.96
2-72-2	Charge	0.500	0.500	-	-	
	Product	0.345	0.343	0.328	0.334	0.92
2-75-3	Charge	-	-	0.500	0.500	
	Product	0.337	0.344	0.334	0.333	0.96
2-75-4	Charge	-	-	0.500	0.500	
	Product	0.333	0.354	0.329	0.333	0.92

[‡] The reactions were catalyzed with 5 mole percent HCl, based on organic acid, and run at 45° for 159 to 160 hours.

TABLE VI

EQUILIBRIUM: METHYL ACETATE AND PROPANOIC ACID

	Catalyst		Sample	Time,		Average		Average
Reactants	Formula	Mole Percent	Number	Hours	K_e	K_e	Deviation	Deviation
$CH_3CO_2CH_3$ + $CH_3CH_2CO_2H$	HCl	5	2-75-1	159	0.96		+0.02	
			2	159	0.92		-0.02	
$CH_3CH_2CO_2CH_3$ + CH_3CO_2H	HCl	5	3	160	0.96		+0.02	
			4	160	0.92		-0.02	
						0.94		0.02
$CH_3CO_2CH_3$ + $CH_3CH_2CO_2H$	HCl	5	1-35-1	167	0.95		+0.01	
			2	167	(0.84)		(-0.10)	
			3	168	0.95		+0.01	
$CH_3CH_2CO_2CH_3$ + CH_3CO_2H	HCl	5	4	211	0.93		-0.01	
			5	212	(0.88)		(-0.06)	
			6	212	0.93		-0.01	
						0.94		0.01
$CH_3CO_2CH_3$ + $CH_3CH_2CO_2H$	$HClO_4$	1	2-49-1	168	0.96		0.00	
			2	168	0.97		+0.01	
$CH_3CH_2CO_2CH_3$ + CH_3CO_2H	$HClO_4$	1	3	169	0.96		0.00	
			4	169	0.97		+0.01	
						0.96		0.005

TABLE VII

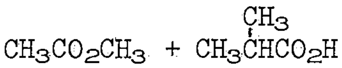
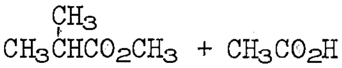
EQUILIBRIUM: METHYL ACETATE AND BUTANOIC ACID

Reactants	Catalyst Formula	Catalyst Mole Percent	Sample Number	Time, Hours	K_e	Deviation
$CH_3CO_2CH_3 + CH_3CH_2CH_2CO_2H$	HCl	5	1	504	0.92	0.00
			2	504	0.92	0.00
$CH_3CH_2CH_2CO_2CH_3 + CH_3CO_2H$	HCl	5	3	505	0.92	0.00
			4	505	(0.84)	(-0.08)

Average K_e = 0.92
Average Deviation = 0.00

TABLE VIII

EQUILIBRIUM: METHYL ACETATE AND 2-METHYLPROPANOIC ACID

Reactants	Catalyst Formula	Catalyst Mole Percent	Sample Number	Time, Hours	K_e	Deviation
 $CH_3CO_2CH_3 + CH_3CH(CH_3)CO_2H$	HCl	5	1	504	(0.74)	(-0.07)
			2	504	0.82	+0.01
 $CH_3CH(CH_3)CO_2CH_3 + CH_3CO_2H$	HCl	5	3	830	0.80	-0.01
			4	830	0.82	+0.01

Average K_e = 0.81
Average Deviation = 0.00

TABLE IX

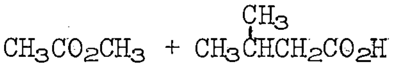
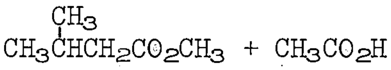
EQUILIBRIUM: METHYL ACETATE AND PENTANOIC ACID

Reactants	Catalyst Formula	Catalyst Mole Percent	Sample Number	Time, Hours	K_e	Deviation
$CH_3CO_2CH_3 + CH_3(CH_2)_3CO_2H$	$HClO_4$	1	1	612	(0.93)	(±0.03)
			2	612	0.90	0.00
$CH_3(CH_2)_3CO_2CH_3 + CH_3CO_2H$	$HClO_4$	1	3	613	0.89	-0.01
			4	613	0.90	0.00

Average K_e = 0.90
Average Deviation = 0.003

TABLE X

EQUILIBRIUM: METHYL ACETATE AND 3-METHYLBUTANOIC ACID

Reactants	Catalyst Formula	Catalyst Mole Percent	Sample Number	Time, Hours	K_e	Deviation
 $CH_3CO_2CH_3 + CH_3\overset{CH_3}{\overset{\vert}{C}}HCH_2CO_2H$	$HClO_4$	1	1	580	0.99	-0.01
			2	580	(1.10)	(+0.10)
 $CH_3\overset{CH_3}{\overset{\vert}{C}}HCH_2CO_2CH_3 + CH_3CO_2H$	$HClO_4$	1	3	580	1.01	+0.01
			4	580	1.00	0.00

Average K_e = 1.00
Average Deviation = 0.007

TABLE XI

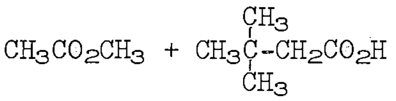
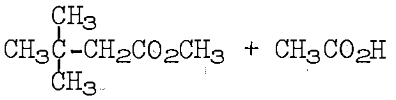
EQUILIBRIUM: METHYL ACETATE AND HEXANOIC ACID

Reactants	Catalyst Formula	Catalyst Mole Percent	Sample Number	Time, Hours	K_e	Deviation
$CH_3CO_2CH_3 + CH_3(CH_2)_4CO_2H$	$HClO_4$	1	1	497	0.92	+0.01
			2	497	0.91	0.00
$CH_3(CH_2)_4CO_2CH_3 + CH_3CO_2H$	$HClO_4$	1	3	497	0.90	-0.01
			4	497	(0.87)	(-0.04)

Average K_e = 0.91
Average Deviation = 0.007

TABLE XII

EQUILIBRIUM: METHYL ACETATE AND 3,3-DIMETHYLBUTANOIC ACID

Reactants	Catalyst Formula	Catalyst Mole Percent	Sample Number	Time, Hours	K_e	Deviation
 $CH_3CO_2CH_3 + CH_3\overset{CH_3}{\underset{CH_3}{C}}-CH_2CO_2H$	$HClO_4$	1	1	770	1.11	
			2	770	1.03	
 $CH_3\overset{CH_3}{\underset{CH_3}{C}}-CH_2CO_2CH_3 + CH_3CO_2H$	$HClO_4$	1	3	770	2.31	
			4	770	2.27	

Equilibrium had not been reached yet after 32 days at 45°.

TABLE XIII

EQUILIBRIUM: METHYL ACETATE AND ACRYLIC ACID

	Catalyst		Sample	Time,		
Reactants	Formula	Mole Percent	Number	Hours	K_e	Deviation
$CH_3CO_2CH_3$ + CH_2=$CHCO_2H$	$HClO_4$	1	1	415	0.82	-0.04
			2	415	0.83	-0.03
CH_2=$CHCO_2CH_3$ + CH_3CO_2H	$HClO_4$	1	3	416	0.89	+0.03
			4	416	0.86	+0.02

Average K_e = 0.86
Average Deviation = 0.03

TABLE XIV

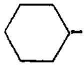
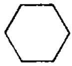
EQUILIBRIUM: METHYL ACETATE AND METHOXYACETIC ACID

	Catalyst		Sample	Time,		
Reactants	Formula	Mole Percent	Number	Hours	K_e	Deviation
$CH_3CO_2CH_3$ + $CH_3OCH_2CO_2H$	$HClO_4$	1	1	451	(0.83)	(+0.06)
			2	452	0.77	0.00
$CH_3OCH_2CO_2CH_3$ + CH_3CO_2H	$HClO_4$	1	3	453	0.79	+0.02
			4	453	0.75	-0.02

Average K_e = 0.77
Average Deviation = 0.02

TABLE XV

EQUILIBRIUM: METHYL ACETATE AND CYCLOHEXANECARBOXYLIC ACID

	Catalyst					
Reactants	Formula	Mole Percent	Sample Number	Time, Hours	K_e	Deviation
$CH_3CO_2CH_3$ +  $-CO_2H$	$HClO_4$	1	1	424	1.03	+0.01
			2	424	1.00	-0.02
 $-CO_2CH_3$ + CH_3CO_2H	$HClO_4$	1	3	425	1.04	+0.02
			4	425	1.01	-0.01

Average K_e = 1.02
Average Deviation = 0.015

TABLE XVI

EQUILIBRIUM: METHYL ACETATE AND CHLOROACETIC ACID

	Catalyst					
Reactants	Formula	Mole Percent	Sample Number	Time, Hours	K_e	Deviation
$CH_3CO_2CH_3$ + $ClCH_2CO_2H$	$HClO_4$	1	1	334	(1.39)	(+0.11)
			2	336	1.28	0.00
$ClCH_2CO_2CH_3$ + CH_3CO_2H	$HClO_4$	1	3	334	1.28	0.00
			4	336	1.27	-0.01

Average K_e = 1.28
Average Deviation = 0.003

TABLE XVII

EQUILIBRIUM: ETHYL ACETATE AND PROPANOIC ACID

Reactants	Catalyst Formula	Catalyst Mole Percent	Sample Number	Time, Hours	K_e	Average K_e	Deviation	Average Deviation
$CH_3CO_2CH_2CH_3$ + $CH_3CH_2CO_2H$	HCl	5	1-83-1	670	(0.89)		(-0.03)	
			2	670	0.92		0.00	
$CH_3CH_2CO_2CH_2CH_3$ + CH_3CO_2H	HCl	5	3	671	0.92		0.00	
			4	671	0.91		-0.01	
						0.92		0.003
$CH_3CO_2CH_2CH_3$ + $CH_3CH_2CO_2H$	$HClO_4$	1	1-57-1	215	0.92		-0.01	
			2	215	0.95		+0.02	
$CH_3CH_2CO_2CH_2CH_3$ + CH_3CO_2H	$HClO_4$	1	3	264	0.92		-0.01	
			4	216	0.95		-0.01	
						0.93		0.013
$CH_3CO_2CH_2CH_3$ + $CH_3CH_2CO_2H$	$HClO_4$	4	3-71-1	261	0.96		0.00	
			2	261	0.95		-0.01	
$CH_3CH_2CO_2CH_2CH_3$ + CH_3CO_2H	$HClO_4$	4	3	262	0.93		-0.03	
			4	262	0.98		+0.02	
						0.96		0.015

TABLE XVIII

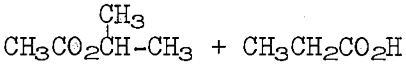
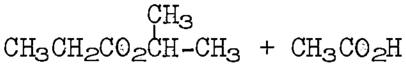
EQUILIBRIUM: PROPYL ACETATE AND PROPANOIC ACID

Reactants	Catalyst Formula	Catalyst Mole Percent	Sample Number	Time, Hours	K_e	Deviation
$CH_3CO_2CH_2CH_2CH_3 + CH_3CH_2CO_2H$	$HClO_4$	1	1	235	1.00	+0.02
			2	235	(1.03)	(+0.05)
$CH_3CH_2CO_2CH_2CH_2CH_3 + CH_3CO_2H$	$HClO_4$	1	3	310	0.97	-0.01
			4	310	0.98	-0.00

Average K_e = 0.98
Average Deviation = 0.01

TABLE XIX

EQUILIBRIUM: METHYLETHYL ACETATE AND PROPANOIC ACID

Reactants	Catalyst Formula	Catalyst Mole Percent	Sample Number	Time, Hours	K_e	Deviation
 $CH_3CO_2\overset{\overset{CH_3}{\vert}}{C}H-CH_3 + CH_3CH_2CO_2H$	$HClO_4$	1	1	287	0.94	+0.01
			2	287	(0.90)	(-0.03)
 $CH_3CH_2CO_2\overset{\overset{CH_3}{\vert}}{C}H-CH_3 + CH_3CO_2H$	$HClO_4$	1	3	288	0.93	0.00
			4	288	0.93	0.00

Average K_e = 0.93
Average Deviation = 0.003

TABLE XX

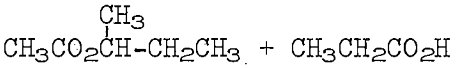
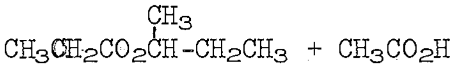
EQUILIBRIUM: BUTYL ACETATE AND PROPANOIC ACID

Reactants	Catalyst Formula	Catalyst Mole Percent	Sample Number	Time, Hours	K_e	Deviation
$CH_3CO_2CH_2(CH_2)_2CH_3 + CH_3CH_2CO_2H$	$HClO_4$	1	1	141	(0.95)	(-0.04)
			2	141	0.99	0.00
$CH_3CH_2CO_2CH_2(CH_2)_2CH_3 + CH_3CO_2H$	$HClO_4$	1	3	142	1.00	-0.01
			4	142	0.99	0.00

Average K_e = 0.99
Average Deviation = 0.003

TABLE XXI

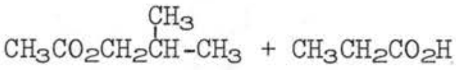
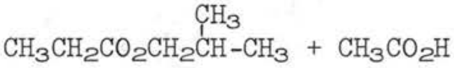
EQUILIBRIUM: 1-METHYLPROPYL ACETATE AND PROPANOIC ACID

Reactants	Catalyst Formula	Catalyst Mole Percent	Sample Number	Time, Hours	K_e	Deviation
 $CH_3CO_2CH(CH_3)\text{-}CH_2CH_3 + CH_3CH_2CO_2H$	$HClO_4$	1	1	500	0.94	0.00
			2	500	0.93	-0.01
 $CH_3CH_2CO_2CH(CH_3)\text{-}CH_2CH_3 + CH_3CO_2H$	$HClO_4$	1	3	501	0.96	+0.02
			4	501	(0.99)	(+0.05)

Average K_e = 0.94
Average Deviation = 0.01

TABLE XXII

EQUILIBRIUM: 2-METHYLPROPYL ACETATE AND PROPANOIC ACID

Reactants	Catalyst		Sample Number	Time, Hours	K_e	Deviation
	Formula	Mole Percent				
 $CH_3CO_2CH_2\overset{\overset{CH_3}{\vert}}{C}H\text{-}CH_3 + CH_3CH_2CO_2H$	$HClO_4$	1	1	454	0.95	0.00
			2	288	0.97	+0.02
 $CH_3CH_2CO_2CH_2\overset{\overset{CH_3}{\vert}}{C}H\text{-}CH_3 + CH_3CO_2H$	$HClO_4$	1	3	454	0.95	0.00
			4	288	0.95	0.00

Average K_e = 0.95
Average Deviation = 0.005

described in the experimental section. This nearly anhydrous (0.0070% H_2O) acetic acid containing perchloric acid was mixed in equimolar quantities with anhydrous butyl propanoate. After 48 hours at 45°, there was <u>no</u> acid exchange.

Two mole percent water was added to the anhydrous acetic acid-perchloric acid. The acetic acid was then mixed with butyl propanoate exactly as before. After 48 hours at 45° the exchange had gone to 73 percent of the equilibrium value.

In a control experiment on an undried acetic acid-perchloric acid solution with the same butyl propanoate under identical conditions, the value calculated for the equilibrium constant was 0.99.

In a similar experiment the "anhydrous" perchloric acid-acetic acid solution (0.0015% H_2O) was divided into three parts. One part was the control. Two mole percent ethanol was added to the second part, and two mole percent water was added to the third part. Each of the three parts were mixed in equimolar amounts with anhydrous ethyl propanoate. After 24 hours at 45°, the anhydrous system had not reacted at all. The extent of reaction calculated for the control was 0.03 percent; for the water the value was 7.7 percent and for the ethanol the value was 7.0 percent.

Another one mole percent perchloric acid-acetic acid solution was dried over Linde AW-500 molecular sieve. It was used with butyl propanoate as before. No acid exchange took place in 48 hours at 45°.

Thus, a 200-fold difference was observed in the reactivity of both butyl propanoate-acetic acid and ethyl propanoate-acetic acid when either water or alcohol was added to the anhydrous system.

A possible explanation for the failure to exchange in the anhydrous system might be the absence of hydronium ions, H_3O^+; however, Kolthoff and Bruckenstein (27) showed that perchloric acid in anhydrous acetic acid was about one-half ionized to the ion pair $CH_3CO_2H_2^+$ amd ClO_4^-. Therefore, with a maximum fifty percent difference in protonated acetic acid one would not expect so great a difference in reactivity.

Thus, it was shown that anhydrous acids and esters do not exchange even in the presence of perchloric acid. Addition of either water or alcohol initiates this reaction. Water or alcohol are nearly equal in starting this reaction. This strongly suggests that the acidolysis of esters is a combination of the two simultaneous reactions, ester hydrolysis and acid esterification.

Catalysts

The chemical literature lists several catalysts that promote the acid exchange of esters. Many of these materials were investigated in this work. Other catalysts tried were a few of those claimed to catalyze similar reactions. Table XXIII gives a complete list of catalysts tried.

Of the catalysts studied, perchloric acid was much more active than any of the others. Trimble and Richardson (39) reported it to be a very active esterification catalyst. For the

TABLE XXIII

CATALYSTS IN ACIDOLYSIS OF BUTYL PROPANOATE WITH ACETIC ACID[‡]

Sample Number	Catalyst	Catalyst Concentration, Mole Percent	Added H_2O Mole Percent	$\frac{\text{Ester II}}{\text{Ester I}} \; \frac{\text{Acid II}}{\text{Acid I}}$	Remarks
3-65-1	HCl	1.0	-	0.0002	
3-61-1	HCl	1.0	2.0	0.004	
2-29-1	HCl	5.0	-	0.026	
3-60-1	HCl	5.0	2.0	0.137	
2-29-4	HCl	10.	-	0.133	The acetic acid was saturated with HCl
3-65-2	HCl-$AlCl_3$	1.0	-	0.0002	$AlCl_3$ did not dissolve
3-65-3	HCl-NaCl	1.0	-	0.0002	NaCl did not dissolve
3-66-1	HCl-Na_2SO_4	1.0	-	0.0006	Na_2SO_4 did not dissolve
2-29-2	$HClO_4$	1.0	2.0	0.99	
2-34-1	$HClO_4$	1.0	-	0.0001	$HClO_4$-acetic acid solution dried over molecular sieves
3-29-1	$HClO_4$	1.0	-	0.005	$HClO_4$-acetic acid solution dried with acetic anhydride.
3-36-1	$HClO_4$	1.0	2.0	0.74	Water added back to #3-29-1
3-33-1	$HClO_4$	1.0	2.0	0.96	Water added back to #3-29-1. Sample went an extra 24 hours.
2-29-3	H_2SO_4	1.0	-	0.258	
3-58-1	H_2SO_4	1.0	2.0	0.313	

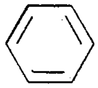
XXIII (Continued)

Sample Number	Catalyst	Catalyst Concentration, Mole Percent	Added H_2O Mole Percent	$\frac{\text{Ester II}\ \ \text{Acid II}}{\text{Ester I}\ \ \text{Acid I}}$	Remarks
3-59-1	p-$CH_3C_6H_4SO_3H$	1.0	2.0	0.137	
2-34-2	$ClSO_3H$	1.0	-	0.057	
2-31-2	C_5H_5N	1.0	-	0.0001	
2-34-3	C_5H_5N	10.0	-	0.0001	
2-34-4	$BF_3 \cdot (C_2H_5)_2O$	1.0	-	0.0001	
2-31-1	CH_3CO_2Na	1.0	-	0.0001	
2-59-1	$HgSO_4$	1.0	-	0.0001	$HgSO_4$ did not dissolve
3-29-2	$ZnCl_2$	1.0	-	0.0001	$ZnCl_2$ did not dissolve
3-36-2	$ZnCl_2$	1.0	2.0	0.0001	$ZnCl_2$ did not dissolve

‡The reactants were equimolar quantities of butyl propanoate and acetic acid. The reaction was run for 48 hours at 45°.

acidolysis of butyl propanoate by acetic acid, perchloric acid was three times as effective as sulfuric acid.

With two moles of water per mole of acid catalyst present in the reaction mixture, the following order of catalytic power was observed:

$HClO_4 > H_2SO_4 > CH_3$--$SO_3H > HCl$

This is the same order as given for acid strength by Hammett (17).

Acid strength is not the only factor affecting catalysis of acidolysis of esters. Hammett stated that strongly electrophilic halides such as boron fluoride, aluminum chloride or zinc chloride may be quite as acidic as strong acids (18). Sowa (36) found zinc chloride and boron fluoride to be more effective catalysts than sulfuric acid for acidolysis of esters. Hydrogen chloride in the presence of $AlCl_3$ is a very strong acid; however, none of these combinations were effective catalysts for acidolysis of esters at 45° in an anhydrous system. Zinc chloride was not effective even in the presence of two mole percent water.

Cantels and Billinger (5) found that salts having an anion in common with the acid catalyst, when added to acetic acid-ethanol solution, promoted the formation of esters and increased the apparent equilibrium constant of the reaction. In the present work the effect of added sodium chloride on the hydrogen chloride catalyzed acidolysis of butyl propanoate by acetic acid was tested; no acidolysis was observed.

An increased reaction rate <u>was</u> observed when sodium sulfate was present during hydrogen chloride catalyzed acidolysis of butyl propanoate by acetic acid. This increase was probably due to the formation of sulfuric acid by the reaction

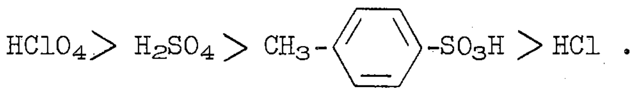
$$2HCl + Na_2SO_4 \rightleftharpoons H_2SO_4 + 2NaCl \; .$$

Sulfuric acid had been shown to be considerably more effective than hydrogen chloride for catalysis of acidolysis.

Sodium acetate, which was reported to catalyze the alcoholysis reaction, was tried in the acidolysis reaction (11). Pyridine was also reported as a catalyst for alcoholysis (40) and reported by other workers to retard esterification (3). Neither sodium acetate or pyridine promoted the acidolysis of esters.

Mercuric sulfate has also been described as an effective catalyst for the acidolysis of some esters (12). At 45°, it did not promote acidolysis of butyl propanoate by acetic acid.

In summary, the acidolysis of esters at 45° required the presence of either water or alcohol to initiate the reaction. Strong protonic acids catalyzed this reaction. The catalytic efficiency followed the order of acid strength:



Effect of Catalyst Concentration

When variations in catalyst and catalyst concentration were made the equilibrium constant remained the same within experimental error. Table XXIV illustrates this fact.

In the methyl acetate-propanoic acid system the catalyst was changed from five mole percent hydrogen chloride to one mole

TABLE XXIV

VARIATION OF EQUILIBRIUM CONSTANT WITH CATALYST CONCENTRATION

Reactants	Initial Mole Ratio Ester/Acid	Catalyst	Catalyst Concentration Mole Percent	K_e[‡]
$CH_3CO_2CH_3$ + $CH_3CH_2CO_2H$	1.0	HCl	5.0	0.94
	1.0	$HClO_4$	1.0	0.96
$CH_3CO_2CH_2CH_3$ + $CH_3CH_2CO_2H$	1.0	HCl	5.0	0.92
	1.0	$HClO_4$	1.0	0.93
	1.0	$HClO_4$	4.0	0.93
	0.5	$HClO_4$	0.5	0.94

[‡] Each equilibrium constant reported is an average of four separate determinations.

percent perchloric acid. The values obtained for the equilibrium constant were 0.94 and 0.96, respectively.

In the ethyl acetate-propanoic acid system, the catalyst was varied from five mole percent hydrogen chloride to 0.5 mole percent, one mole percent and four mole percent perchloric acid. The K_e values were 0.92, 0.94, 0.93 and 0.93, respectively. These values are all within experimental error of ±0.02.

Effect of Initial Reactant Concentrations

As illustrated in Table XXV, when the initial ester-to-acid ratio was changed from 0.5 to 2.0 in the perchloric acid catalyzed reaction of ethyl acetate and propanoic acid the observed equilibrium constant changed from 0.94 to 1.00. This deviation is greater than experimental error and believed to be real. Thus, a six percent deviation has been observed for K_e for a fourfold change in initial ester-to-acid ratio.

This deviation was not expected when this work was started. Such deviation was not observed for alcoholysis of esters by Juvet and Wachi (26); however, Juvet and Wachi made only a threefold change in initial reactant concentrations and were not dealing with acidolysis.

Trimble and Richardson (38) reported a linear relationship between the observed equilibrium constant and the catalyst concentration for the esterification reactions. Corso and Durruty (6) and others have reported variation in the equilibrium constant with change in the reactant concentrations for esterification.

TABLE XXV

VARIATION OF EQUILIBRIUM CONSTANT WITH INITIAL CONCENTRATION OF REACTANTS[‡]

Reactants	Mole Ratio Ester:Acid	Sample Number	K_e	Average K_e	Deviation	Average Deviation
$CH_3CO_2CH_2CH_3$ + $CH_3CH_2CO_2H$	1:2	1	(1.00)		(+0.06)	
		2	0.94		0.00	
$CH_3CH_2CO_2CH_2CH_3$ + CH_3CO_2H	1:2	3	0.93		-0.01	
		4	0.96		+0.02	
				0.94		0.01
$CH_3CO_2CH_2CH_3$ + $CH_3CH_2CO_2H$	2:1	1	1.00		0.00	
		2	0.99		-0.01	
$CH_3CH_2CO_2CH_2CH_3$ + CH_3CO_2H	2:1	3	1.00		0.00	
		4	(0.93)		(-0.07)	
				1.00		0.003

[‡] The samples were run for 450 hours at 45° with 0.5 mole percent $HClO_4$ based on organic acid charged.

Therefore, if acidolysis is actually alternating esterification and hydrolysis reactions, one should not expect a constant value for the observed equilibrium constant for acidolysis over wide ranges of catalyst and reactant concentrations.

Effect of Variation of Carboxylic Acid Moiety

One of the intentions of this work was to correlate the electronic or steric factors with the equilibrium constant for the acidolysis of esters. No correlation has been found.

Examination of Table XXVI illustrates a complete lack of correlation between pK values for acids and their displacing tendency in acidolysis of methyl acetate. Acids of greater acidity (lower pK values) than acetic have equilibrium constants both above and below unity for the acidolysis reaction. The same is true of acids of less acidity (higher pK values) than acetic acid.

A somewhat better correlation can be made between the acid displacing tendency and the Hammett σ values where the σ value is a measure of electron donating or electron withdrawing power of the substituent (20,25). This correlation is certainly not completely acceptable because Hammett's values were derived for aromatic compounds. The present acidolysis work deals with a completely aliphatic system; however, this is the only correlation found that even partially agrees with the observed data.

The equilibrium constant could not be correlated with degree of steric hindrance. For example isovaleric acid is quite similar to isobutyric acid in structure.

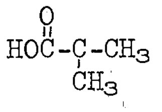
TABLE XXVI

VARIATIONS IN DISPLACING TENDENCY OF CARBOXYLIC ACIDS IN ACIDOLYSIS OF METHYL ACETATE

Acid	Acidolysis K_e (45°)	Acid[‡] pK (25°)	Hammett[‡‡] σ Value
Methoxyacetic	0.77	-	-0.268
2-Methylpropanoic	0.81	4.86	-0.151
Acrylic	0.86	4.26	-
Pentanoic	0.90	4.84	-0.151
Hexanoic	0.91	4.86	-0.161
Butanoic	0.92	4.82	-0.151
Propanoic	0.96	4.88	-0.170
3-Methylbutanoic	1.00	4.78	-0.115
Acetic	1.00	4.76	0.000
Cyclohexanecarboxylic	1.02	4.90	-
Chloroacetic	1.28	2.87	+0.226

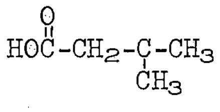
[‡] All values calculated from Kortune, Vogel and Andrusow (29) or from Dippy, Hughes, and Laxton (10).

[‡‡] Hammett values were taken from Jaffe (25) for substituents in the para position.



$HO\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}-CH_3$

Isobutyric



$HO\overset{\overset{O}{\|}}{C}-CH_2-\underset{\underset{CH_3}{|}}{C}-CH_3$

Isovaleric

If one considers Newman's (31) "Rule of Six" as a measure of steric hindrance, then isovaleric acid which has a six number equal to six is more highly hindered than isobutyric acid which has a six number of zero. In the acid exchange of isovaleric acid with methyl acetate the equilibrium constant was equal to 1.00. The observed equilibrium constant for the isobutyric acid exchange was 0.81. Thus, the more highly hindered isovaleric acid has a greater tendency to displace acetic acid from methyl acetate than does less hindered isobutyric acid. The equilibrium constants for other aliphatic acids and methyl acetate falls within these two values.

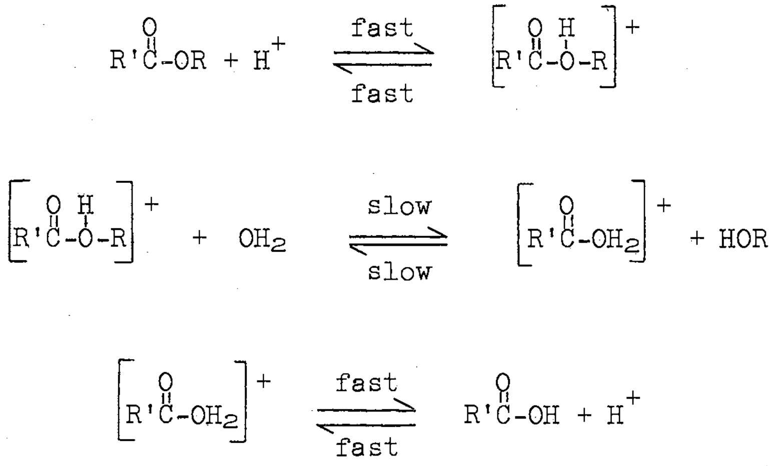
In summary, no completely satisfactory correlation has been found to predict the displacing tendency for a carboxylic acid in the acidolysis of esters. Hammett's σ values give a fair approximation to a correlation for the acid displacing tendency and the observed equilibrium constant. Acetic acid substituted with substituents of electron withdrawing power tend to displace acetic acid from acetic esters. Acetic acid substituted with substituents of electron donating power tend to be displaced by acetic acid in their esters.

Effect of Variation of the Alkyl Moiety

Table XXVII summarized the trend observed with structural changes in the acidolysis of alkyl acetates by propanoic acid. As the alkyl chain is lengthened from one to four carbon atoms the equilibrium constant decreases slightly for ethyl and then approaches unity for normal butyl. Branching on the alkyl chain causes a slight shift to the acetate form of the ester.

Proposed Mechanism for Acidolysis

One possible mechanism for the acidolysis of esters is analogous to the mechanism of acid-catalyzed hydrolysis of esters suggested by Datta, Day and Ingold (8). Ingold (24) included this mechanism as a general one and termed it $A_{Ac}2$ in his textbook. The steps of this mechanism are as follows:



$$R'\overset{O}{\overset{\|}{C}}\text{-}OR + H^+ \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} \left[R'\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\overset{|}{O}}\text{-}R\right]^+$$

$$\left[R'\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\overset{|}{O}}\text{-}R\right]^+ + OH_2 \underset{\text{slow}}{\overset{\text{slow}}{\rightleftharpoons}} \left[R'\overset{O}{\overset{\|}{C}}\text{-}OH_2\right]^+ + HOR$$

$$\left[R'\overset{O}{\overset{\|}{C}}\text{-}OH_2\right]^+ \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} R'\overset{O}{\overset{\|}{C}}\text{-}OH + H^+$$

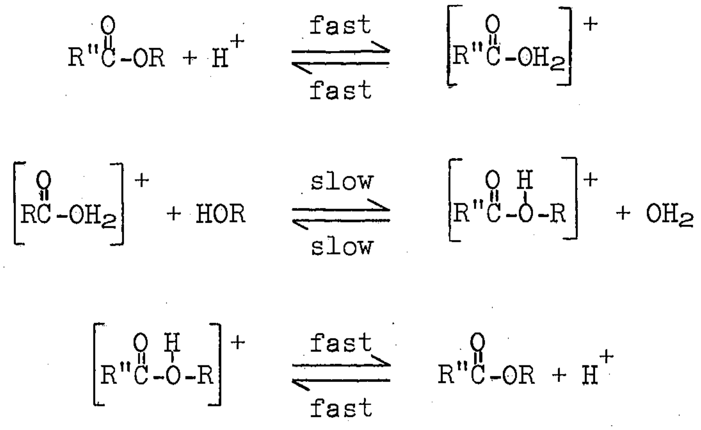
TABLE XXVII

EFFECT OF ALKYL STRUCTURE ON ACIDOLYSIS OF ALKYL ACETATES BY PROPANOIC ACID

Alkyl	R	K_e (45°C)	Average Deviation
Methyl	CH_3-	0.96	0.005
Ethyl	CH_3CH_2-	0.93	0.01
Propyl	$CH_3CH_2CH_2$-	0.98	0.01
1-Methylethyl	$(CH_3)_2CH$-	0.93	0.003
Butyl	$CH_3CH_2CH_2CH_2$-	0.99	0.003
1-Methylpropyl	$CH_3CH_2CH(CH_3)$-	0.94	0.01
2-Methylpropyl	$CH_3CH(CH_3)CH_2$-	0.95	0.005
1,1-Dimethylethyl[‡]	$(CH_3)_3C$-	-	-

[‡] The t-butyl ester decomposed extensively when heated in the presence of perchloric acid.

These steps in reverse constitute esterification.



$$R''\overset{O}{\overset{\|}{C}}\text{-OR} + H^+ \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} \left[R''\overset{O}{\overset{\|}{C}}\text{-OH}_2\right]^+$$

$$\left[R\overset{O}{\overset{\|}{C}}\text{-OH}_2\right]^+ + \text{HOR} \underset{\text{slow}}{\overset{\text{slow}}{\rightleftharpoons}} \left[R''\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\overset{|}{O}}\text{-R}\right]^+ + OH_2$$

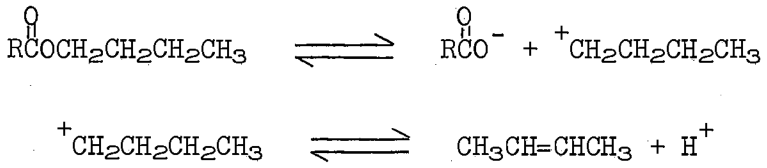
$$\left[R''\overset{O}{\overset{\|}{C}}\text{-}\overset{H}{\overset{|}{O}}\text{-R}\right]^+ \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} R''\overset{O}{\overset{\|}{C}}\text{-OR} + H^+$$

A second mechanism which seems equally applicable was proposed by Day and Ingold (9) for the esterification of acids. This mechanism involves attack of the hydrogen ion on the acyl oxygen. Basically this is the same mechanism except a proton is later transferred to the alkyl-linked oxygen.

Opinions of authoritative workers in physical organic chemistry differs on the best choice for the mechanism of acid catalyzed hydrolysis of esters. Hine (21) favors the hydrogen ion attack on the acyl oxygen. Gould (16) favors the hydrogen ion attack on the alkyl-linked oxygen. We have no basis for preferring one over the other. Both mechanisms require either water or alcohol in the reaction. Both would presumably involve ester hydrolysis alternating with acid esterification as the mechanism for acidolysis of esters.

The $A_{Ac}2$ mechanism is chosen over the $A_{Ac}1$ (unimolecular) because it has the general characteristics of a bimolecular mechanism rather than a unimolecular mechanism. That is, the acidolysis is dependent on concentration of water or alcohol and the rates of the acidolysis are very sensitive to steric retardation. These characteristics were described by Ingold (24) to be indicative of the bimolecular mechanism.

Sowa (36) had earlier proposed a carbonium-ion mechanism for this reaction that explained his experimental observations. In studying the acidolysis of *n*-butyl propionate with acetic acid he observed that a significant amount (10 percent) of *n*-butyl groups were converted to *s*-butyl groups. He observed similar results with isobutyl propionate. Sowa's procedure consisted of heating the ester with a mixture of acetic acid and acetic acid-boron trifluoride complex to 100° for one hour. In order to explain the formation of the rearranged product, a splitting of the alkyl-oxygen bond of the ester was proposed.



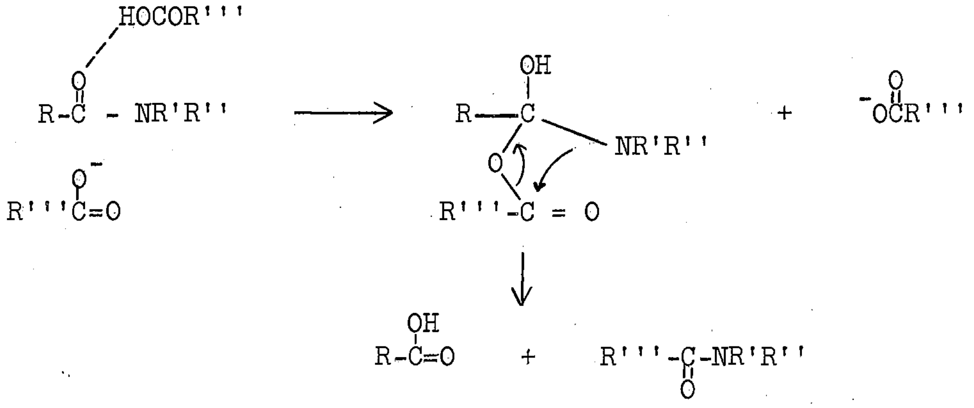
$$R\overset{\overset{O}{\parallel}}{C}OCH_2CH_2CH_2CH_3 \rightleftharpoons R\overset{\overset{O}{\parallel}}{C}O^- + {}^+CH_2CH_2CH_2CH_3$$

$${}^+CH_2CH_2CH_2CH_3 \rightleftharpoons CH_3CH{=}CHCH_3 + H^+$$

The rearranged olefin was then supposed to react with the organic acid to give the new ester. Evidence for this reaction mechanism was the formation of isopropyl acetate from propylene and acetic acid in the presence of sulfuric acid. No rearranged products have been observed in our work. The use of G.C. for analysis of reaction mixtures would permit detection of rearranged products in less than one percent concentrations.

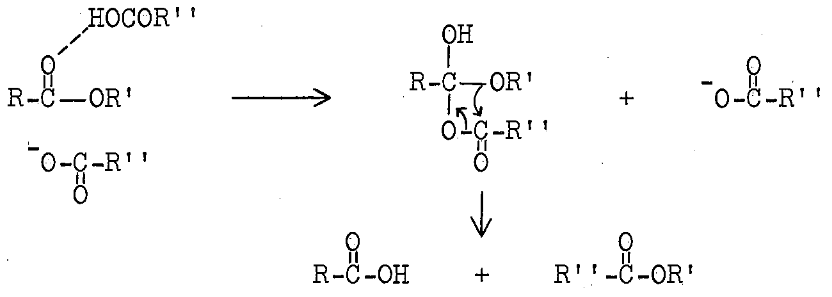
The only rearranged products observed in the course of this work was the dissociation of *t*-butyl acetate to isobutylene and acetic acid. This decomposition was so fast that it was impossible to make measurements of acidolysis in the reaction of t-butyl acetate with propanoic acid.

A reaction mechanism proposed by Ring and coworkers (35) for the uncatalyzed acid exchange on N,N-disubstituted carboxamides may be applicable to acid exchange on esters. In this reaction the carboxamide is protonated by a hydrogen ion from the organic acid and then attacked at the acyl carbon by the anion of the acid.



Rearrangement of the intermediate is described as a four-center-type reaction such as those discussed by Hine (22).

This type of mechanism seems plausible for the uncatalyzed acid exchange on esters. Thus



It is less attractive for the reaction catalyzed by strong acids because these would suppress ionization of the carboxylic acid. More importantly, this mechanism does not account for the apparently essential role of either water or alcohol in the acidolysis of esters.

Most of the past acidolysis work was done in such a way that contaminating water may have promoted the reaction. For example, Sowa (36) refluxed his reaction mixture in an open condenser. In the Barkenbus (4) work, a catalyst was used that contained one molecule of water per molecule of catalyst. Most, if not all, of the work of Gault and Chablay (14,15,7) was done in sealed glass tubes; however, at 175° a different mechanism may be in operation.

In the reaction mechanism that now is most reasonable, two reactions are taking place alternately. In one step water is reacting with a protonated ester. In the next step alcohol is reacting with a protonated acid. If the water reaction is the faster of the two, then there should be a net build-up of alcohol during the reaction. If the esterification reaction is faster there should be a net build-up of water during the reaction.

In the acidolysis of butyl acetate with propanoic acid, very good alcohol-ester separation was obtained. When the product was examined only a trace of butyl alcohol could be found. Therefore, one would suspect that the esterification reaction is faster than the hydrolysis reaction. This is in good agreement with rate studies for hydrolysis and esterification of esters. Trimble and Richardson (39) reported for the reaction

$$C_2H_5OH + CH_3CO_2H \rightleftharpoons CH_3CO_2C_2H_5 + H_2O$$

(with one normal perchloric acid catalysis) an esterification rate constant of 0.00074 and a hydrolysis rate constant of 0.00018.

More evidence is needed before the mechanism of the acidolysis of esters is fully explained; however, on the basis of the evidence observed, it appears that the acidolysis of esters at 45° proceeds by way of alternating ester hydrolysis and acid esterification. The $A_{Ac}2$ mechanism of Ingold and coworkers (8,9) seems applicable.

SUMMARY

A gas chromatographic technique has been developed for analyzing a reaction product containing a mixture of esters and carboxylic acids. This technique was then used to determine equilibrium constants of the acidolysis reaction for a series of carboxylic acids and esters.

At temperatures up to 45°, acidolysis of esters do not occur in an anhydrous system even in the presence of strong mineral acid catalysts. At these conditions the acid exchange of esters may be initiated by either water or alcohol. These are nearly equally effective.

Proton-donating acids catalyze the acidolysis of esters. The effectiveness of the acid catalysts follows the order of acid strength.

A fourfold variation in catalyst concentration did not affect the value of the equilibrium constant for acidolysis of esters. A fourfold variation in the ratio of starting materials caused a six percent change in equilibrium constant in the one instance studied.

No satisfactory correlation has been found between various carboxylic acids and their tendency to displace acetic acid from acetic esters. This tendency cannot be correlated with the degree of steric hindrance nor can this tendency be correlated with the displacing acid's pK values.

As the alkyl chain length in acetate esters increases, the equilibrium constant approaches unity. Branching on the alkyl chain tends to decrease slightly the value for the equilibrium constant.

A mechanism is proposed for the acidolysis of esters that follows that proposed by Ingold and coworkers for the two separate reactions of acid-catalyzed esterification of acids and acid-catalyzed hydrolysis of esters.

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