Studies on alcoholysis. I. Dilatometric determination of the velocity of alcoholysis in the presence of a large excess of alcohol.

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The replacement of radicals in esters by the action of an alcohol containing a different alkyl group has long occupied the attention of many chemists. This replacement is very slight unless the esters and alcohols are heated for a long time in sealed tubes, but occurs fairly rapidly in the presence of strong acids or alkalies.

Friedel and Crafts (*Annalen*, 1864, *130*, **198**; 1865, *133*, 207) noticed this interchange of groups when they heated ethyl acetate with amyl alcohol or amyl acetate with ethyl alcohol.

Claisen (*Ber.* 1887, *20*, 646), while studying the action of sodium methylate on benzaldehyde, found that the product of the reaction when acidified with acetic acid and fractionated gave a tolerable yield of methyl benzoate. This he attributed to the replacement of the benzyl group in benzyl benzoate, first formed, by the methyl group under the action of sodium methylate. As a very small amount of sodium brings about this interchange, he assumed the existence of an intermediate compound, which can decompose in two ways according to conditions.

Purdie and his co-workers (*J. 0. S. Trans* 1886, *47*, 862 ; 1887, *51*, 627 ; and 1888, *53*, 301) studied the interchange in the esters of acetic acid. In the presence of sodium alcoholate, the inter-change is fairly rapid, but, they state that even in the absence of that reagent and at ordinary temperature, the reaction occurs. According to them more complex radicals have a greater affinity for the acid than the less complex except methyl, which has an affinity higher than ethyl, but lower than amyl. Greater affinity of the more complex radicals has also been noticed by Rose (*Annalen*, 1880, *205*, 210) in his study of the esters of carbonic acid. On the other hand, Bertoni and Truffi (*Gazetta*, 1881, *14*, 23) arrived at just the contrary results while studying the action of different alcohols on amyl nitrite.

Patterson and Dickinson (*J. C. S., Tran* . 1901, *79*, 280) boiled for a few hours ethyl tartrate with methyl alcohol containing 5% hydrogen chloride. By measuring the rotation of the mixture they found that nearly 87% was changed into methyl tartrate, while in the reverse case, the change was nearly

Kremann (*Monatsh.* 1905, *26*, 783 and 1908, *29*, 23) studied the action of alcoholic sodium hydroxide on tri-acetine, and found that with a quantity of caustic soda equivalent to 3% of that required for complete saponification the velocity of the interchange of radicals is too rapid for measurement. If the quantity of the alkali be varied from 0·29 to 2·9 % there is a variation in the velocity of alcoholysis with variation in the quantity of caustic soda used, though direct proportionality was not established. It is suggested that an equilibrium occurs between the ester and alcohol and that this is accelerated by the catalytic action of the alkali.

Sudborough and Davies (*Proc. Chem. Soc.* 1905, *21*, have shown that, although the ethyl esters of most substituted benzoic acids can be transformed into methyl esters by boiling their solutions in methyl alcohol with a small quantity of sodium methoxide, the reaction does not proceed when the ester is di-ortho-substituted.

Bruni and Contardi (*Atti. R. Accd. Lincei*, 1906, (V), *15*, *i.*, 837) examined the action of an optically active alcohol on certain esters in the absence of a catalyst and attempted to determine velocity constant by means of polarimetric measurements.

Pfanl (*Monatsh.* 1910, *31*, 301) studied the interchange of methyl, ethyl and propyl radicals in the esters of terepthalic, benzoic and oxalic acids under the action of the alkali. He denies the catalytic character of the alkali and favours the view of the formation of an intermediate compound. By taking advantage of the fact that dimethyl terephthalate is far more insoluble in methyl alcohol than the corresponding diethyl or dipropyl esters, he was able to show that a rough proportionality exists between the velocity of the interchange and the amount of the alkali used.

Leuchs and Theodoresen (*Ber.* 1910, *43*, 1239) were able to replace the ethyl group in ethyl malonate by methyl by using a 0·1 N. solution of ammonia in methyl alcohol.

See also in this connection :—

Weddige (*J. Pr. Chem.* 1875, (ii), *12.* 434) ;
Salomon (*Ber.* 1875, 8, 1506) ;
Bachmann (*Annalen*, 1883, *218*, 50) ;
Israel (*Annalen*, 1885, *231*, 229).
Conrad and Epstein (*Ber.* 1887, *20*, 3052) ;
Peters (*Ber.* 1887, *20*, 3318) ;
Kossel and Kruger (*Zeit. Physicl. Chem.* 1891. *15*, 321);
Skraup (*Monatsh.* 1893, *14*, 479);
Henriques (*Zeit. Angew. Ghem.* 1898, 338) ;
Haller (*Compt. rend.*, 1906, *143*, 657) ;
Reid (*Amer. Chem.* J, 1909, *41*, 483) ;
Telemachos Komnenos (*Monatsh.* 1911, *32*, 77).

From a review of the above it will be seen that although the fact, that extensive interchange of radicals in mixtures of esters and alcohols occurs in the presence of alkalies or acids, is confirmed by a number of workers, no systematic attempt, with the exception of the experiments of Bruni and Contardi, has yet been made to determine the velocity with which this interchange occurs in mixtures of different esters and alcohols or the relation between the influence of alkalies and acids on this interchange. The object of the present research has been to determine the velocity of alcoholysis under the influence of acids and alkalis. The method selected was the dilatometric. This method had already been used for studying analogous reactions, *e. g.*, hydrolysis of esters and bioses.

Koelichen (*Zeitsch. Physikal Chem.*, 1901, *33*, 154) used the change of volume to determine the velocity with which diacetonyl alcohol decomposes into acetone in the presence of sodium hydroxide. Benrath (*ibid*, 1909, *67*, 501) studied the density changes of liquid systems in which chemical reactions occur ; for example, the inversion of cane sugar and formation and hydrolysis of esters. He came to the conclusion that the density changes of a system run parallel to the changes in the concentration of the reacting substances.

Galleoti (*ibid*, 1911, *76*, 105 and 1912, *80*, 241) investigated dilatometrically the inversion of cane sugar and the hydrolysis and synthesis of esters, sugars and similar bodies, in the presence of acids or enzymes. Recently Wright, (*Proc. Ghem.*

SOC. 1913, *29*, 280,) and Anderson and Holden (*J. Physical Chem.* 1914, *18*, 152) employed this method for following the course of the hydrolysis of cane sugar.

I. General Experimental.

I have studied the action of methyl, ethyl, propyl, *iso*propyl, *iso*butyl, and *iso*amyl alcohols on esters of acetic, propionic, butyric, benzoic, monochloracetic, and trichloracetic acids. All these materials were obtained from Kahlbaum. Ethyl and methyl alcohols were treated three times with small quantities of calcium and distilled, and their purity tested by taking their densities. Further treatment with calcium produced no alteration in their densities. The other alcohols were purified by treating them once with calcium and then distilling.

The esters were generally found slightly acidic. Contact with anhydrous sodium carbonate for some time did not remove the acidity except in the case of esters of mono-and tri-chloroacetic acids. With other esters the addition of about 1 per cent of water enabled sodium carbonate to remove the acidity in the course of one or two days. They were then dried over calcium chloride and carefully fractionated until they distilled within half a degree.

The volume changes observed were found to be very small, being less than 0·4% of the volume of the reacting mixture in the most favourable cases, while in many cases they were less than 0·1%. A reading microscope was therefore used and by this means the level of the meniscus in the capillary could he read to within 0·1 mm. Further, the great coefficient of expansion of the reacting substances necessitated a very delicate adjustment of the temperature of the thermostat. The thermostat was heated electrically, the regulator used being of a type described in *Tran. Faraday Soc.* 1911, 7, 249. By using a very efficient stirrer and by keeping the platinum contacts in the regulator quite clean the temperature of the bath could be kept constant within 1/100th of a degree, while smaller variations were read on a Beckmann thermometer, and a volume correction applied.

All the reactions were studied at a temperature of 30°. In the absence of a catalyser the reaction mixtures gave no appreciable change of volume even after keeping them for a week except a mixture of ethyl trichlor-acetate and methyl alcohol. 17cc. of this mixture contracted about 0·006 cc. in the course of a week. In all cases therefore, the reactions were studied under the influence of a catalyser. An alcoholic solution of hydrogen chloride approximately 0·02N was mostly used, while a few reactions were also studied with sodium alcoholate as the catalyser.

With a view to determine whether the variation in the concentration of the reacting substances is a linear function of the change of density of the reacting system the densities of the following mixtures were carefully determined:—

(1) 1 mol. of ethyl benzoate + 2 mol. of methyl alcohol.

(2) 0·6 mol. of ethyl benzoate + 0·4 methyl benzoate + 0·4 ethyl alcohol + 1'6 methyl alcohol.

(3) 0·4 mol. of ethyl benzoate + 0·6 methyl benzoate + 0·6 ethyl alcohol + 1·4 methyl alcohol.

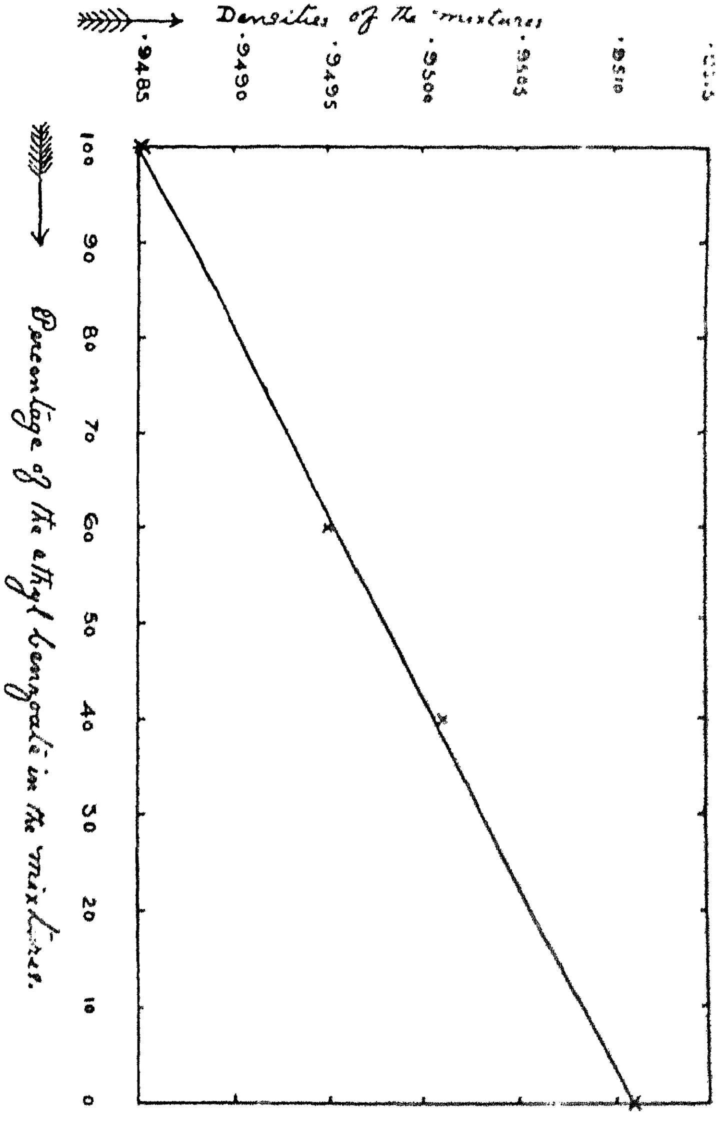
(4) 1 mol. of methyl bezoate + 1 mol. of ethyl alcohol + 1 mol. of methyl alcohol.

The pyknometer was similar to the one used by Homfray *(J. G. S., Trans* 1905, *87,* 1430).

The internal diameter of the capillary was about 0·4 mm. The bent limb had only one mark near the bend, while on the straight limb a number of marks 1mm. apart were etched and tbe capacity of the etched portion very carefully assertained; Each division had a capacity of 0·2 c. mm. A piece of rubber tubing pushed on the open end of the bent portion and slightly pinched facilitated the adjustment of the liquid to the mark near the bend and its position in the other limb was read by a magnifying glass on the etched portion. To prevent evaporation both the open ends were fitted with ground glass caps which were only removed when adjusting and reading the level. The capacity of the bulb was about 8 cc. and the density was determined correctly to within 2 units in the fifth place.

In the accompanying curve the ordinates represent the densities of the different mixtures and the abscissae the corresponding fall in the concentration of ethyl benzoate which is replaced by methyl benzoate. Tbe values He approximately on a straight line which shows that the change in the concentration of ethyl benzoate is a linear function of the change in the density of the system within the limit of experimental error.

Owing to the great difficulty of carrying out these density determinations no others were made, and in what follows it has been assumed in all cases that the concentration change is a linear function of the density change. In any case the variation from this rule would probably be too slight to affect reaction velocity results.


Densities of the mixtures
·9485
·9490
·9495
·9500
·9505
·9510
·9515
100
90
80
70
60
50
40
30
20
10
0
Percentage of the ethyl benzoate in the mixtures.

In studying the velocities of alcoholysis the dilatometers used were of two kinds (1) those having bulbs with 2 capillaries and taps (2) those with bulbs having one capillary and tap.

The length of the capillary between the bulb and the tap was about 30 to 40 cm., and the internal diameter about 0·8 mm. In each case a mark was etched near the tap and each dilatometer was carefully calibrated and the capacity of different portions of the capillary exactly ascertained.

Dilatometers of the first type were used when the proportion of alcohol to ester was limited (1 : 1, 1 : 2 etc). and the reaction was studied as a bimolecular one. The results of these experiments will be communicated later.

When a large excess of alcohol was used it was thought that the reaction would probably approximate to a unimolecular one and, as a knowledge of the volume of the reacting mixture at the beginning is not absolutely essential in such a case, dilatometers of the second type were used in these experiments and the results are recorded in the present paper.

On account of the excess of the alcohol in the reaction mixture the relative amount of ester is too small to give a measurable change in volume with dilatometers of 15cc. capacity. For these reactions dilatometers of 50 to 70cc. capacity were used. The increase in the capacity of the dilatometer introduced, no doubt, a larger error duo to temperature variation of the bath, but the advantage secured by having a greater change in volume more than compensated for this. As these dilatometers had no side tubes the following method of filling them was adopted: A requisite amount of alcohol containing the catalyser was cooled about 10° below the temperature of the bath. An approximate amount of the required ester was then added, the exact amount added being found by rapidly weighing the mixture. The dilatometer was thoroughly evacuated, the end of the capillary dipped in the mixture and the tap opened, the liquid rushed in and filled the bulb in about 2 minutes, leaving only a small bubble of air. The dilatometer was then transferred to the bath and the expansion of the liquid due to the rise in the temperature was usually found not only sufficient to fill the bulb completely, but also the whole of the capillary. The level of the liquid was then adjusted to a convenient height by a narrow capillary. In about 80 minutes temperature equilibrium was established and then readings were taken at suitable intervals. The time of the first reading was taken as the starting point.

It was necessary to ascertain whether, at the temperature of the bath, the hydrogen chloride used as a catalyser had any action on the alcohols or esters. Action of mineral acids on alcohols has already been studied by a few workers, but only at higher temperatures.* Several dilatometers were filled with alcohols or esters containing a small amount of hydrogen chloride and the change in the level of the liquid noted Ethyl benzoate and ethyl acetate containing hydrogen chloride (approximately 0·2N) were kept in the bath for a week and the variation in the level was found to be less than 1 mm. The action of the gas on other esters was not studied. Alcohols gave an appreciable change in volume with hydrogen chloride and the following table summarises the results obtained. I he dilatometers used were of different capacities and the bores of the capillaries were also slightly varying. They are, however, reduced to the volume 13·8cc. and bore of the same size to afford facility of comparison.

TABLE 1.

	Alcohol.	Con. of HC1.	Duration of the reaction in days.	Vol. of the reaction Mis.	Rise in cm.	Increase of Vol. in cc.
1	Methyl ...	0·704 N	71	13·8cc	35·68	0·1612
2		0·358 N	,,	,,	17·9	0·0811
3	Ethyl ...	0·36 N	,,	,,	5·11	0·02315
4	,,	0·56 N	24	,,	1·86	0·00802
5	Propyl ...	0·36 N	,,	,,	1·64	0 00718
6	Isoamyl ...	0·36 N	,,	,,	1·14	0·0051

In the first three cases the liquid in the dilatometer after the last reading had been taken was transferred to a flask and the strength of the acid determined by titration.

The concentration in the first case was found to have fallen to 0.26 N ; in the second case tc 0.120 N; in the third case to 0.286 N. The increase in volume thus seems to be due to the combination of the alcohol with the acid. In 71 days about 63% of hydrogen chloride has combined with methyl alcohol, while with ethyl alcohol only about 20 per cent.

The action of hydrogen chloride on *iso*butyl and *iso*-propyl alcohols was also studied. The results obtained are not given in the above table, as the strength of the acid used had

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*Cain (*Zeitsch Physikal Chem* 1893, *12.* 751) ;
Villiers (*Ann. Chim. Phys.* 1880, (V), *21, 72*).

not been accurately ascertained. The increase in volume in these cases is also small being less than that given by alcohol under the same conditions.

From the first two results it appears that the increase in volume caused by the action of hydrogen chloride on methyl alcohol is practically proportional to the concentration of the acid used. These experiments were used to determine what part of the variation in volume obtained in alcoholysis was due to the action of the hydrogen chloride on the alcohol. As a further check the dilatometers were kept in the thermostat often more than a week after the reaction due to alcoholysis was completed, in order to ascertain the action of hydrogen chloride alone on the mixture. The variation thus determined was usually a little less than that calculated. The necessary correction was then introduced. The correction is appreciable in the case of methyl alcohol but is so small as to be negligible when other alcohols are used.

The following example will show the correction made in such cases and the method of arriving at the amount of correction to be introduced.

Mixture of ethyl acetate and methyl alcohol in the ratio 1 : 20 and with hydrogen chloride 0·0213 N as catalyst.

Time hours mins.	Actual reading in mm.	Corrected reading.
0·0	249·3	249·3
1·35	219·8	219·8
2·5	213·2	213·1
3·5	204·3	204·2
4·5	198·9	197·7
19·15	185·8	185
67·35	187·8	
115·5	189·7	

From the numbers in column two it is clear that the alcoholysis has reached a state of equilibrium within 20 hours. The rise observed in the last two values is due to the action of the hydrogen chloride on the alcohol and amounts to about 1 mm. in 24 hours.

The readings given in the third column are corrected on the above basis. It will be seen that the corrections are very small and in all cases where the alcoholysis is comparatively

• rapid and the concentration of the catalyser small, the same holds good. It is only in the case of the esters of trichloroacetic acid and of benzoic acid that the corrections become really appreciable.

In the above series of experiments the correction was controlled by comparing the result with the changes actually observed by the action of hydrogen chloride on methyl alcohol under similar conditions. The change calculated from the observed readings was 1·4 for the first 24 hours. This value is somewhat higher than that obtained by the first method but the difference would not affect the constants in the great majority of the determinations made.

II. Alcoholysis as a unimolecular Reaction with Hydrogen Chloride as catalyser

It seemed probable that the simplest type of reaction would be that in which the alcohol was in large excess of the ester. With a constant amount of catalyst in solution the reaction should approximate to a unimolecular one, at least in the initial stages. If so, the expression $1/t$. log. $a/a-x$ (where a is proportional to the initial concentration of the ester and x to the amount changed in time t) should be constant, and the following results show that this is the case.

In most of the experiments the ester was mixed with about 20 mols. of the requisite alcohol. With the above ratio of ester to alcohol the reaction reaches an equilibrium when about 96% of the ester is transformed and for a strict application of the above formula a greater proportion of alcohol would have been desirable. But even with the above ratio the total change in many cases is as low as 0·05% of the volume of the reacting mixture. Greater dilution, therefore, was scarcely practicable. In one case, however, the proportions 40 : 1 were used and it was found that the constant differed only slightly from that obtained with 20 mols. As the methyl esters are denser than the other esters, a contraction occurs when methyl alcohol reacts with the esters of other alcohols. Similarly there is always an expansion in volume when a methyl ester reacts with other alcohols.

Effect of Varying the Concentration of the catalyser.

The concentration of the catalyser employed during all these experiments was not quite identical, but varied within a small limit. By assuming that there is a direct proportionality between the concentration of the catalyser used and the value of the constant, all the constants are recalculated for 0·02N strength of the catalyser. That we are justified in making this assumption will he seen from the following experiments in which a mixture of flso-butyl acetate and 20 mols. of methyl alcohol was allowed to undergo a change under the influence of the catalyser of varying concentration.

The temperature was 29.96°, and in *(a)* the concenration of the catalyser was 0.0101 N and in *(b)* 0.0298 N.

t (in mins)	d.	a—x	1/t log a/a-x	t (in mins)	d.	a—x	1/t log a/a-x
0	211·2	152·2	...	0	203·9	119·6	...
60	190·1	131·1	0·00108	30	180·9	96·6	0·00309
120	172·1	113·1	0·00107	60	162·7	78·4	0·00306
180	157	98	0·00106	120	135·6	31·3	0·00306
240	144	85	0·00105	180	118·2	33·9	0·00304
360	122·8	63·8	0·00105	300	99	14·7	0·00304
*inf.	59	...		inf.	84·3	...	...

Mean value of the constant 0·00106 j Mean value of the constant 0·00306

As the concentration of the catalyser increases from 0.0101 N to 0.0298N the value of the constant also rises from 0.00106 to 0.00306. The rise in the value of the constant is thus proportional to the rise in the concentration of the catalyser within the limits of experimental error.

The following tables, Nos. 1 to 19, give the values for $1/t \log_{10} a/a-x$ obtained with different esters and alcohols.

R= Molecular ratio of alcohol to ester;
T= Temperature;
C= Concentration of catalyser;
V= Volume of dilatometer in cc.;
Cp= Capacity of 1 cm. length of the capillary in cc. and
d= Distance in mm. of meniscus from a fixed mark.

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* The value of *d* at *t.* =inf. were obtained by allowing the mixtures fco stand until the only alteration in volume was that due to the action of the hydrogen chloride on the methyl alcohol. The value was checked in several cases by a process of extrapolation.

1. Ethyl Acetate and Alethyl Alcohol.

(a)

R=20, T=30·01, C=0·02178
V=29·19, Cp=0·002006

R=20, T=30·02, C=0·0
V=59·23, Cp=0 004447

t (in mins)	d	a—x	1/t log a/a-x	t (in mins)	d.	a—x	1/t log a/a-x
0	244	64·0		0	249·3	64·3	
90	215·6	35·6	0·00283	95	219·8	34·8	0·00281
120	208·7	28·7	0·00290	125	213·1	28 1	0·00268
150	203·5	23·5	0·00290	185	204·2	19·2	0·00284
210	196·3	16·3	0·00283	245	197·7	12·7	0·00268
270	190·6	10·6	0·00289	inf.	185·0		...
inf.	180·0	...	...				

R=20, T=29.96, C=0.01973 V=50.05, Cp=0.004513

t (in mins)	d.	a—x	1/t log a/a-x
0	194·4	52·4	
50	180·6	38·6	0·00265
140	164·9	22·9	0·00257
200	158·3	16·3	0·00253
320	149·8	7·8	0·00258
inf.	142·0		

Mean values ... (a)= 0·00287; (b)= 0·00285; (c) = 0·00258

Corrected for 0·02N HCl (a) = 0·00263; (b)= 0·00268; (c) =

K= 0 00264.

2. Propyl Acetate and Methyl Alcohol.

R=20, T=29·98, C=0·02106, V=72·77 Cp=0·004603.

t(in mins)	d.	a—x	1/t log a/a-x
0	277·8	149·8	0·00244
15	225·7	137·7	0·00252
36	209·5	121·5	0·00255
75	184·4	96·4	0·00254
95	173·9	85·9	0·00246
150	152·1	54·1	0·00249
210	133·0	45·0	0·00248
270	120·1	32·1	
inf.	88·0		...

Mean = 0·002495. Reduced to 0·02 N HCl=0·00237.

3. iso-Propyl Acetate and Methyl Alcohol.

R=20, T=30, C=0·0229 V=46·41, Cp=0·004543

t (in mins)	d.	a—x	1/t log a/a-x
0	244	146·7	
25	235·1	137·8	0·00109
55	225·3	128·0	0·00108
115	207·6	110·3	0·00108
192	188·7	91·4	0·00107
222	182·2	84·9	0·00107
252	176·4	791	0·00106
312	166·7	69·4	0·00104
432	149·7	52·4	0·00104
inf.	97·3	...	

Mean value=0·001065, reduced to 0·02 1ffHCl=0·00093

4. iso-Butyl Acetate and Methyl Alcohol.

R=20, T=30·03, C=0·0216, V=46·41, Cp=0·004543.

t (in mins)	d.	a – x	1/t *log* a/a-x
0	231·1	129·1	...
60	196·0	94·0	0·00229
120	170·4	68·4	0·00230
180	151·9	49·9	0·00229
240	138·4	36·4	0·00229
300	128·5	26·5	0·00229
497	111·4	9·4	0·00229
inf.	102	...	...

Mean value=0·00229, reduced to 0·02 N HCl = 0·00210

5. iso-Amyl Acetate and Methyl Alcohol.

(a)

=20, T=30·05, C=0·02068
V=46·41, Cp=0·004543.

(b)

R=40, T=30, C=0·02336,
Cp=0·004603.

t (in mins)	d.	a—x	1/t log a/a-x	t (in mins)	d.	a—x	1/t log a/a-x
0	244·5	110·0	...	0	255·5	92.1	...
60	215·4	80.9	0·00222	25	242·7	79·3	0·00260
120	193·9	59·4	0·00223	55	229·0	65·6	0·00268
180	177·8	43·3	0·00225	100	213·5	50.1	0·00264
240	166·3	31·8	0·00224	160	198.5	35·1	0·00262
435	146·6	12·1	0·00220	220	188·2	24·8	0·00259
inf.	134·5	...		280	181·15	17·75	0·00255
				340	175·4	12.0	0·00260
				550	167·1	3·7	0·00254
				inf.	163·4		

Mean=0·00223, reduced to
0·02 NHCl=0·00215.

Mean=0·002602, reduced to
0·02 NHCl=0·00223.

6. iso-Butyl formate and Methyl Alcohol.

=20, T=29.99, C=0·02184, V=56·56, Cp=0·00 l<271

t(in mins)		a-x	1/t log a/a-x
0	232·4	77·2	...
8	219·2	64·0	0·0102
18	206·0	50·8	0·0101
28	194·4	39·2	0·0105
38	185·6	30·4	0·0106
48	180·3	25·1	0·0102
73	168·9	13·7	0·0103
103	161·5	6·3	0·0106
inf.	155·2		

Mean value=0·01035, reduced to 0·02 N HCl=0·0948.

7. Ethyl Propionate and Methyl Alcohol.

R=20, T=30, C=0·02434,

t(in mins)	d	a-x	1/t log a/a-x
0	238·7	89·7	
31	227·1	78·1	0·00194
00	217·9	68·9	0·00191
90	208·1	59·1	0·00201
120	200·0	51·0	0·00204
150	193·4	44·4	0·00204
210	183·0	34	0·00201
inf.	149·0		...

Mean value=0·00199, reduced to 0·02 N HCl = 0·00163.

8. Ethyl Butyrate and Methyl Alcohol.

0, T=30·01, C=0·02402, V=29·19, Cp=0·002006.

t(in mins)		a-x	1/t log a/a-x
0	244·3	102·3	
100	222·0	80·0	0·00107
135	215·3	73 3	0·00107
196	205-0	63·0	0·00107
255	197·2	552	0·00105
318	189·1	47·1	0·00106
553	167·8	25·8	0·00108
1215	147·4	5·4	0·00105
inf.	142·0	...	...

Mean value=0·00106, reduced to 0·20 N HCl=0·000886.

9. Ethyl Monochloracetate and Methyl Alcohol.

=20, T=29·99, C=0·02142, V=50·05, Cp=0·004543.

t(in mins)		a-x	1/t log a/a-x
0	230·9	78·4	
30	224·8	72·3	0·00117
60	219·2	66·7	0·00117
90	214·2	61·7	0·00115
150	204·5	52·0	0·00119
210	197·6	45·1	0·00114
330	185·7	33·2	0·00113
575	170·3	17·8	0·00112
inf.	152·5	...	...

Mean value = 0·00115, reduced to 0·02 N HCl = 0·00108.

10. Ethyl Trichloracetate and Methyl Alcohol.

R = 20, T = 30, C = 0·02292, V = 72·77, Cp = 0·004603.

t(in mins)	d.	a-x	1/tlog a/a-x
0	246·2	148·2	
240	237·4	139·4	0·000111
1100	209·5	111·5	0·000112
2600	171·7	73·7	0·000117
4075	148·0	50·0	0·000116
5500	1321	341	0·000116
6860	122·3	24·3	0·000114
inf.	98	...	...

Mean value = 0·000114, reduced to 0·02 N HCl = 0·0000995.

11. Ethyl Benzoate and Methyl Alcohol.

R = 20, T = 29·99, C = 0·0228, V = 59·23, Cp = 0·004447.

t(in mins)	d.	a-x	1/t log a/a-x
0	210.8	100·1	...
1880	204·3	94·1	0·0000194
4320	193·3	831	0·0000187
8695	179·5	69·3	0·0000184
13080	168·3	58·1	0.0000181
21695	151·7	41·5	0·0000176
30320	139·8	29·6	0·0000175
inf.	110·2		...

Mean value = 0·0000183, reduced to 0·02 N HCl = 0·0000161.
*

12. Methyl Acetate and Ethyl Alcohol

0, T=29·98, C=0·02196, V=59·23, Cp=

t(in mins)	d.	a-x	1/t log a/a-x
0	179·8	39·9	
45	183·1	36·6	0·000833
120	187·9	31·8	0·000822
180	191·3	28·4	0·000802
240	194·2	25·5	0·000809
360	1991	20·6	0·000804
1170	215·5	4·2	0·000835
inf.	219·7	...	

Mean value=0·000819, reduced to 0·02 N HCl=0·000741

13. Methyl Acetate and Propyl Alcohol.

=20, T=29·98, C=0·0317, V=59·23, Cp=0·000447.

t(in mins)	d.	a-x	1/t log a/a-x
0	173·4	56·1	
90	181·2	48·3	0·000723
210	189·7	39·8	0·000701
415	201·6	27·9	0·000731
1130	220·7	8·8	0·000712
inf.	229·5	...	

Mean value =0·000719, reduced to 0·02 N HCl=0·000454.

14. Methyl Acetate and *iso*-Propyl Alcohol.

R=20, T=29·98, C=0·0214, V=29·96, Cp=0·002006

t(in mins)	d.	a-x.	1/t log a/a-x
0	172·3	89·7	
2885	190·0	72·0	0·0000331
5800	204·7	57·3	0·0000336
8655	216·4	45·8	0·0000337
26370	250·7	11·3	0·0000341
inf.	262·0		...

Mean value=0·0000336, reduced to 0·02 N HCl=0·0000314

15. Methyl Acetate and *iso*-Butyl Alcohol.

(a)

R=20, T=30, C=0·02342
V=46·41, Cp=0·004543

•• R=20, T=30, C=0·02342
V=72·77 Cp=0·004543

t(in mins)	d	a-x	1/t log a/a-x	b (in mins)	d	a-x	1/t log a/a-x
0	151·5	58·0		0	198·8	87·6	
122	157·7	51·8	0·000402	120	208·2	78·2	0·000401
240	162·7	46·8	0·000388	240	215·8	70·6	0·000390
360	167·6	41·9	0·000392	420	226·1	60·3	0·000386
1240	190·6	18·0	0·000392	1285	258·5	27·9	0·000387
1746	198·0	11·5	0·000402	1790	269·7	16·7	0·000402
inf.	209·5	...	...	inf.	286·4		...

Mean value=0·000395.　　　　Mean value=0·000393

Value of (a) and (b) reduced to 0·02 N HCl=0·000337

16. Methyl Acetate and *iso*-Amyl Alcohol.

(a)

R=20, T=29·97, C=0·02492
V=59·23, Cp=0·004447

(6)

R=20, T=29·27, C=0·02492
V=29·19, Cp=0·002006

t(in mins)	d	a-x	1/t log a/a-x	t(in mins)	d	a-x	1/t log a/a-x
0	179·8	27·2	...	0	175·9	29·1	
120	183·0	24·0	0·000453	900	193·8	11·2	0·000460
975	197.0	10.0	0·000446	1380	198·7	6·3	0·000481
1455	201·7	5·3	0·000488	inf.	205·0	...	...
inf.	207·0	...	...				

Mean value=0·000462　　　　Mean value=0·000471

Mean value (a) and (b) reduced *to* 0·02 N HCl=0·000374

17. Methyl Propionate and Ethyl Alcohol.

R=20, T=30, C=0·02342, V=72·77, Cp=0.004603

t (in mins)	a	a-x	1/t log a/a-x
0	194·4	72·0	
60	198·7	67·3	0·000488
180	207·7	58·3	0·000509
300	215·6	50·4	0·000516
428	222·0	44·0	0·000500
1240	248·2	17·8	0·000490
1720	255·6	10·4	0·000488
inf.	266	...	...

Mean value=0·000498, reduced to 0·02 N HCl=0·000425.

18. Methyl Butyrate and Ethyl Alcohol.

R=20, T=29·99, C=0·02314, V=50·05, Cp=0·004543.

t(in mins)	d	a-x	1/t log a/a-x.
0	191·7	50·3	...
60	193·6	48·4	0·000280
300	200·5	41·5	0·000278
1120	217·0	25·0	0·000271
1600	223·4	18·6	0·000270
2535	231·6	10·4	0·000270
inf.	242·0	...	...

Mean value=0·000274, reduced to 0·02 N HCl=0·000237.

19. Methyl Monochloracetate and Ethyl Alcohol.

R=20, T=29·99, C=0·0214, V=51·41, Cp=0·004536.

t (in mins)	d.	a-x	1/t log a/a-x
0	148·4	64·6	
270	164·4	48·6	0·000458
520	174·7	38·3	0·000437
1195	193·5	19·5	0·000435
2590	208·4	4·6	0·000443
inf.	213	...	...

Mean value = 0·000443, reduced to 0·02 N HCl = 0·000414.

20. Influence of Water on Alcoholysis with Hydrogen Chloride

Ethyl Acetate and Methyl Alcohol (with a little water)

(a) R=20, T=29·96, C=0·01971, , V=72·77, Cp=0·004603

(b) R=20, T=29·97, C=0·2194, *W=0·5364%, V=72·77, Cp=0·004603

t.	d.	a-x	1/t log a/a-x	t.	d,	a-x	1/t log a/a-x8
0	227·3	78·1	...	0	214·3	77·3	...
40	214·4	65·2	0·00196	60	201·5	64·0	0·00137
100	198·4	49·2	0·00200	151	186·0	48·5	0·00134
190	182·4	33·2	0·00195	211	177·7	40·2	0·00135
250	175·1	25.9	0·00192	271	171·6	34·1	0·00131
370	164·1	15·1	0·00193	331	165·8	28·3	0·00132
inf.	149·2	...		inf.	137·5		...

Mean value = 0·00195, reduced to 0·02 N HCl=0·00198.

Mean value=0·00134, reduced to 0·02 N HCl=0·00122

The value without water under the same conditions=0·00264.

*W—Concentration of water expressed as percentage.

III. Summary and Conclusions.

The following table gives a summary of the results obtained. The values for the constants are the mean values, corrected for 0·02 N hydrogen chloride, given in the preceding pages and multiplied by the factor 2·3026. In all cases the unit of time is one minute and the temperature 30°.

TABLE II.

Velocity Constants with 0·02 N Hydrogen Chloride as Catalyser

	Description of Mixture.	K.
1.	Ethyl acetate and Methyl alcohol	0·00608
2.	Propyl acetate and Methyl alcohol	0·00546
3.	*iso*-propyl acetate and Methyl alcohol	0·00214
4.	*iso*-Butyl acetate and Methyl alcohol	0·00188
5 (a.)	*iso*-Amyl acetate and Methyl alcohol	0·00495
5 (b.)	*iso*-Amyl acetate and Methyl alcohol	0·00513
6.	*iso*-Butyl formate and Methyl alcohol	0·218
7.	Ethyl propionate and Methyl alcohol	0·00375
8.	Ethyl butyrate and Methyl alcohol	0·00204
9.	Ethyl Monochloracetate and Methyl alcohol	0·00249
10.	Ethyl trichloracetate and Methyl alcohol	0·000229
11.	Ethyl benzoate and Methyl alcohol	0·0000371
12.	Methyl acetate and Ethyl alcohol	0·00172
13.	Methylacetate and propyl alcohol	0·00105
14.	Methyl acetate and *iso*-propyl alcohol	0·0000723
15.	Methyl acetate and *iso*-Butyl alcohol	0·000776
16.	Methyl acetate and *iso*-Amyl alcohol	0·000861
17.	Methyl propionate and Ethyl alcohol	0·000979
18.	Methyl butyratate and Ethyl alcohol	0·000546
19.	Methyl monochloracetate and Ethyl alcohol	0·000953
20 (a.)	Ethyl acetate and Methyl alcohol with 0·138 per cent. of water	0.00456
20 (b.)	Ethyl acetate and Methyl alcohol with 0.536 per cent. of water	0.00281

In all the experiments with the exception of No. 5 (b) the ratio of ester to alcohol was 1 : 20; in 5 (b) it was 1 : 40.

In any discussion of results relating to experiments on alcoholysis, the analogy between alcoholysis on the one hand and esterification and hydrolysis on the other should be borne in mind. In all three cases the first stage probably consists in the formation of an additive compound.

(a) In esterification a compound of alcohol and acid.

(b) In alcoholysis a compound of ester and alcohol.

(c) In hydrolysis a compound of ester and water.

The second stage in the reaction consists in the decomposition of the intermediate compound into

(a) Ester and water (b) Ester and alcohol (c) acid and alcohol.

The function of acids and alkalis as catalysts in all three reactions is presumably of the same type and may consist in the formation of a complex ion, derived from the hydrion or hydroxylion and *one* of the reacting substances or more probably an ion derived from the above mentioned additive compounds and an ion of the catalyst (Jones and Lapworth *Proc. Chem. Soc.* 1914, *30*, 142).

This analogy between the three types of reactions has already been indicated by experimental results. It has been shown that diortho substituted benzoic acids are not readily esterified by the ordinary hydrogen choride method (Ber-1894, *27*, 510, 1580, 3146.) The esters when once formed are not readily hydrolysed (V Meyer Ber. 1895, *28*, 188) and are also not readily transformed into other esters (Sudborough and Davies *Proc. Chem Soc.* 1905, *21*, 87.)

It is also well known that in the absence of a catalyst comparatively strong organic acids are much more readily esterified than weak acids (Sudborough and Lloyd *J. C. S. Trans.* 1899, *75*, 481; Sudborough ibid 1912, *101*, 1235); further that the esters of such acids are usually readily hydrolysed by water alone and still more readily by alkalis (Sudborough and Feilmann *Proc. Chem. Soc.* 1897, *13*, 241) and recent experiments by Sudborough and Bhagvat show that the esters of such acids undergo alcoholysis in the absence of a catalyst much more readily than the esters of feeble acids.

As the result of experiments on the rates of esterification of the normal fatty acids by means of a methyl alcoholic solutions of hydrogen chloride, (Sudborough and Gittins, *J. G. S. Trans.* 1908, 93, 211) have arrived at the following relative numbers :— Acetic : propionic : *n.* butyric as 100 : 88·3 : 48·0. The relative alcoholysis numbers for the ethyl esters of these acids in the presence of methyl alcohol are 100 : 62 : 33·6.

The following are the relative esterification constants of acetic, monochlor-acetic, trichloracetic, and benzoic acids 100: 35·6 : 0 93 : 0·272. (Sudborough and Turner *J. C S. Trans.* 1912 *101*, 237) and the corresponding alcoholysis values for the ethyl esters 100: 41: 3·8: 0·610. The relationship between formic acid and acetic acid is represented by the relative values for the alcoholysis of the *iso*butyl esters with methyl alcohol. They are as 45 : 1, whereas the relative rates of esterification are as 10·8 : 1.

A comparison of all these numbers indicates that the relative rates of esterification by the catalytic method and of alcoholysis of the corresponding esters by means of hydrogen chloride follow the same order *viz.* formic, acetic, propionic, *n*-butyric, trichloracetic, benzoic. Monochloracetic acid, however, forms an exception.

All the values so far compared have been obtained by using hydrogen chloride as catalyst and working in the presence of a relatively large excess of methyl alcohol. It is to he remembered that the esterification constants were determined at 15° and the alcoholysis constant at 30°.

The relative activities of the various alkyl groups calculated from the experiments on alcoholysis of the acetates are methyl 100, ethyl 28, *n*-propyl 19, *iso*propyl 3·4, *iso*butyl 16, and 17.

The *iso*propyl group derived from a secondary alcohol is thus far less reactive than the *iso*butyl and *iso*amyl groups derived from primary alcohols. Comparative numbers based on esterification experiments by the catalytic method are not available. Michael and Wohlgast (*Ber.*, 1907, *48*, 3157) have shown that, using the direct method of esterification and trichloracetic acid as the organic acid, secondary alcohols react much less readily than primary ones.

A comparison of the numbers given in experiments 1 & 12, 7 & 17, 8 & 18 indicate that the ratio ethyl ester+methyl alcohol/methyl ester+ethyl alcohol, that is K/K′ is almost the same for acetates, propionates and butyrates, the ratios being respectively 3·5, 3·8 and 3·7. These numbers indicate that the relative affinities of the methyl and ethyl groups towards an acyl group are to a certain extent independent of the nature of the acyl group.

Hemptinne (*Zeitsch. physikal. Chem.*. 1894, *13*, 562), Lowenherz (ibid 1894, *15*, 389) and J. Meyer (ibid 1909, *66*, 81) have arrived at the same conclusion as the result of experiments on the hydrolysis of methyl, ethyl, propyl and butyl esters with dilute hydrochloric acid. Thus Hemptinne gives the ratio methyl ester / ethyl ester=0·97 and ethyl ester / propyl ester=1·01, as determined by experiments on esters of a few of the normal fatty acids. Somewhat similar results are given by Meyer as the result of working with succinates. The ratio is approximately 1.

With comparatively strong acids, such as chloroacetic and tartaric, the hydrolysis ratio ethyl ester / methyl ester can be somewhat different *e. g.* with tartaric acid the ratio is 0·83 (J. Meyer) and with monochloracetic acid 0·92 (Lowenherz). The results of experiments Nos. 9 & 19 also indicate that the alcoholysis ratio in the case of esters of strong acids (cf. chloracetates) may be somewhat different.

Hemptinne also established the ratios, using dilute hydrochloric acid as hydrolysing agent, acetate ester / propionate ester=1·07 and propionate ester / butyrate ester=1·75. The corresponding alcoholysis values are 1·6 and 1·8. Similarly Lowenherz found the values formate ester / acetate ester=20, acetate ester / monochloracetate ester=1·7 and acetate ester / benzoate ester=190, whereas the alcoholysis values are 45 : 2·4 : 164.

In addition to the experiments described in this paper a number of other reactions have also been studied with different proportions of alcohol and ester and also with sodium alcoholates as catalysts. The results and a further discussion will be given in due course.

In conclusion I have to thank Dr. Sudborough for suggesting the research, Dr. Travers for many valuable suggestions during the course of the experiments and Drs. Sudborough and H. E. Watson for personal direction during the progress of the work.

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