STUDIES IN ACIDOLYSIS:

I The Equilibrium between Acetic Acid, Trichloracetic Acid and their Ethyl Esters

II. The Equilibrium between Acetic Acid, Trichloracetic Acid and their Methyl Esters

By J. J. Sudborough and D. D. Karvé.

I. The Equilibrium between Acetic Acid, Trichloracetic Acid and their Ethyl Esters

INTRODUCTION

Attention has repeatedly been drawn to the analogy between the three processes of esterification, hydrolysis of esters and alcoholysis as represented by the following equations :—

1. $CH_3\cdot CO_2H + C_2H_5OH \longrightarrow CH_3\cdot CO_2C_2H_5 + H_2O$.
2. $CH_3\cdot CO_2C_2H_5 + H_2O \longrightarrow CH_3\cdot CO_2H + C_2H_5\cdot OH$.
3. $CH_3\cdot CO_2C_2H_5 + CH_3\cdot OH \longrightarrow CH_3\cdot CO_2CH_3 + C_2H_5\cdot OH$.

As a rule all three proceed very slowly in the absence of a catalyst and are typical balanced reactions. Thus using equivalent quantities of acetic acid and ethyl alcohol, 66 per cent of the acid is esterified when equilibrium is attained.

In connection with the mechanism of the process of esterification we wished to examine the action of ethyl alcohol on a mixture of acetic and trichloracetic acids. This study is complicated by the possibility of reactions between the acids and esters present in the mixture, e.g. :—

$$CH_3\cdot CO_2C_2H_5 + CCl_3\cdot CO_2H \longrightarrow CH_3\cdot CO_2H + CCl_3\cdot CO_2C_2H_5.$$

Such reactions are termed ACIDOLYSIS. They consist in the replacement of an acyl group, e.g., acetyl, $CH_3\cdot CO$, in an ester by a second acyl group, e.g., trichloracetyl, $CCl_3\cdot CO$, in the presence of the acid derived from the second acyl group, e.g., in the case considered, trichloracetic acid. The reaction is thus analogous to alcoholysis, which consists in the replacement of the alkyl group in a given ester by a second alkyl group in the presence of the alcohol derived from the second alkyl.

As a preliminary to the study of the action of ethyl alcohol on a mixture of acetic and trichloracetic acids we have examined the equilibrium between acetic acid, trichloracetic acid and their ethyl esters.

Reid[1] has already studied several cases of acidolysis, viz. (*a*) benzyl acetate and benzoic acid, and (*b*) ethyl benzoate and *p*-bromobenzoic acid. The method of procedure adopted by Reid was to seal known amounts of the reacting substances in glass tubes and to heat the tubes at relatively high temperatures for definite periods. They were afterwards opened, the free acid neutralized with a dilute solution of sodium carbonate and the proportions of the two esters in the neutral oil ascertained by specific gravity determinations with the aid of a graph showing the variation of the specific gravity with the composition of the mixtures of the two esters.

In this paper Reid discusses the partition of an acid between two alcohols and also the partition of an alcohol between two acids, in other words alcoholysis and acidolysis, and attempts to show that alcoholysis and acidolysis constants can be calculated from the esterification equilibria of the respective acids and alcohols. He regards esterification as the partition of the acyl group, R·CO, between ·OH and ·OEt. If the latter are present in equivalent quantities, i.e. if molecular proportions of acetic acid and ethyl alcohol are used, then the relative amount of acyl combined with ·OH and ·OEt, i.e. the relative concentrations of free acid and ester in the equilibrium mixture is given by the equations—

$$\frac{\text{Ester}}{\text{Acid}} = \frac{66{\cdot}57}{33{\cdot}43} = 1{\cdot}991$$

which is the square root of K, the equilibrium constant given by the equation—

$$\frac{x^2}{(A - x)(B - x)} = K$$

in which A and B are the original concentrations of acid and alcohol and x is the concentration of the ester at equilibrium.

The ratio ester/acid in the equilibrium mixture for original concentrations other than unity is given by the equation—

$$\frac{\text{Ethyl acetate}}{\text{Acid}} = \frac{\text{OEt}}{\text{OH}}\,1{\cdot}991.$$

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[1] *Amer. Chem. J.*, 1911, **45**, 479.

Similarly for acetic acid and methyl alcohol.

$$\frac{\text{Methyl acetate}}{\text{Acid}} = \frac{\text{OMe}}{\text{OH}}\ 2{\cdot}281$$

and for the alcoholysis equilibrium of methyl and ethyl acetates

$$\frac{\text{Methyl acetate}}{\text{Ethyl acetate}} = \frac{\text{OMe}}{\text{OEt}} \times \frac{2{\cdot}281}{1{\cdot}991}$$

Miss J. E. Minor, in a dissertation (Bryn Mawr College, 1917) on 'A Study of the Equilibrium in the Alcoholysis of Esters,' criticizes Reid's conclusions and claims that his formula holds good only when the equilibrium constant for the particular alcoholysis is nearly unity and when the ratio of the concentrations of the reacting substances is also approximately unity.

Miss Minor claims that the alcoholysis equilibrium constant, $K_{\text{alc.}}$ is the ratio of the esterification equilibrium constants $K_{\text{est.1.}}$ and $K_{\text{est.2.}}$ for the given acid with the alcohols 1 and 2, and, as the esterification equilibrium constants for the same acid with alcohols of similar constitution do not vary widely, it follows that, for an alcoholysis reaction where the two alkyl radicles are of a similar character, the equilibrium constant cannot be far from unity.

Similar relationships should hold good for the acidolysis equilibrium constant and the esterification equilibrium constants of the given alcohol with the two acids.

In the particular case we have examined, namely, acetic and trichloracetic acids with ethyl alcohol, the esterification equilibrium constants are very similar, namely, 66·57 and 74·00[1] and hence the acidolysis equilibrium constant should be practically unity.

The method adopted by Reid for estimating the amounts of the two esters in mixtures of the acids and esters cannot be used in the reaction we have studied, as the esters of trichloracetic acid are readily hydrolized by alkalis. The method we have adopted is based on the following facts:—

1. The free acids can be determined by titration with standard ammonium hydroxide solution using methyl red, rosolic acid or litmus as indicator.

2. The ethyl trichloracetate can be estimated by titration with standard sodium (or barium) hydroxide using phenolphthalein as

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[1] Lichty, *Amer. Chem. J.*, 1896, **18**, 590.

indicator.[1] In determining this ester in mixtures containing the free acids and their ethyl esters the difference between the results of titrations 1 and 2 will give the amount of standard alkali required to hydrolize the ethyl trichloracetate.

3. By adding excess of standard sodium hydroxide solution to the mixture, allowing to stand for several hours, usually 12, until saponification is complete, and then titrating the excess of alkali with standard hydrochloric acid using phenolphthalein as indicator and then subtracting from the total amount of alkali required for complete neutralization and saponification the amount required in titration 2, the quantity required for saponifying the ethyl acetate is obtained.

The two acids used in these experiments have the following dissociation constants :—

Acetic acid $K = 0{\cdot}0018$[2]
Trichloracetic acid $K = 121{\cdot}0$[2]

The reaction :—

$$CCl_3{\cdot}CO_2H + CH_3{\cdot}CO_2Et \rightleftharpoons CCl_3{\cdot}CO_2Et + CH_3{\cdot}CO_2H$$

has been studied by determining the starting and equilibrium concentrations of the following mixtures :—

1. Ethyl acetate and trichloracetic acid.
2. Ethyl trichloracetate and acetic acid.
3. Ethyl acetate, acetic acid and trichloracetic acid.
4. Ethyl acetate, acetic acid and ethyl trichloracetate.
5. Ethyl trichloracetate, acetic acid and trichloracetic acid.
6. Ethyl trichloracetate, ethyl acetate and trichloracetic acid.
7. All four.

In all seven mixtures the substances were taken in practically equimolecular proportions, but, as the equilibrium point was found to be very nearly the composition represented by mixture No. 7, an eighth experiment was made with all four substances but using a larger proportion of trichloracetic acid.

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[1] Lichty, *Amer. Chem. J.*, 1895, **17**, 28 ; Sudborough and Lloyd, *J. Chem. Soc.*, 1899, **75**, 482.

[2] *Zeitsch. Physikal. Chem.*, 1899, **3**, 176.

The results of the eight determinations give results varying from 0·98 to 1·08 with a mean value of 1·02 for the equilibrium constant, i.e.

$$\frac{\text{Trichloracetic acid} \times \text{ethyl acetate}}{\text{Ethyl trichloracetate} \times \text{acetic acid}} = 1{\cdot}02$$

where the concentrations of the substances are expressed in gram molecules.

This value 1·02 may be taken as equal to unity as the difference is within the experimental errors involved in the processes employed. It therefore follows that the velocity constants k_1 and k_2 of the two reactions—

(1) $CCl_3{\cdot}CO_2H + CH_3{\cdot}CO_2Et \longrightarrow CCl_3{\cdot}CO_2Et + CH_3{\cdot}CO_2H$
(2) $CH_3{\cdot}CO_2H + CCl_3{\cdot}CO_2Et \longrightarrow CH_3{\cdot}CO_2Et + CCl_3{\cdot}CO_2H$

are equal and may be represented by k.

The values of k/V have been calculated from the data given in Tables I and II (p. 11) in order to ascertain the order of magnitude of this constant.

In the general case of a reaction of the second order, where all four substances are originally present in the molecular proportions indicated in the equation

$$\underset{A}{CH_3{\cdot}CO_2Et} + \underset{B}{CCl_3{\cdot}CO_2H} \rightleftarrows \underset{C}{CCl_3{\cdot}CO_2Et} + \underset{D}{CH_3{\cdot}CO_2H}$$

when x molecules have reacted the concentrations are respectively $A-x$, $B-x$, $C+x$ and $D+x$
and hence,

$$\frac{dx}{dt} = k_1 (A-x)(B-x) - k_2 (C+x)(D+x)$$
$$= x^2 (k_1 - k_2) - x\,[(A+B)\,k_1 + (C+D)\,k_2] + ABk_1 - CDk_2.$$

In the case represented in Table II this equation is much simplified as $A=B$, $C=D=O$ and $k_1 = k_2$.

Hence $\frac{dx}{dt} = A^2 k - 2\,A\,kx.$

and if $V=$ volume of 1,000 grams of mixture and A_1 the number of gram molecules per 1,000 grams,

$$A = \frac{A_1}{V} \text{ and } x = \frac{x_1}{V}$$

$$\text{and } \frac{dx}{dt} = \frac{A^2{}_1}{V}\,k - \frac{2A_1}{V}\,kx_1$$

integrating

$$kt = \frac{V}{2A_1} \ln \frac{A_1}{A_1 - 2x}$$

$$k = \frac{V}{2A_1 t} \ln \frac{A_1}{A_1 - 2x}$$

$$\frac{k}{V} = \frac{1}{2A_1 t} \ln \frac{A_1}{A_1 - 2x}$$

assuming that V does not change appreciably during the course of the reaction.

EXPERIMENTAL

1. PREPARATION OF PURE SUBSTANCES

(*a*) *Acetic acid.*—Kahlbaum's pure glacial acid was repeatedly frozen in ice and the liquid was poured off. After repeating this process for half a dozen times, the acid was finally distilled. Very nearly the whole of it distilled at constant temperature. A second distillation gave the pure acid boiling at 115·5—116° at 681 mm.

(*b*) *Ethyl acetate.*—The ester absorbed moisture very rapidly on exposure to the atmosphere and the last traces of moisture as well as those of alcohol were only removed after repeated distillations, over calcium chloride and potassium carbonate, into receivers connected with calcium chloride tubes. The pure ester boiled at 73·5 – 74° at 682 mm.

(*c*) *Trichloracetic acid.*—The acid was in the form of a colourless hygroscopic solid, mixed with a slightly brownish heavy liquid. The melting point was not at all sharp. It was distilled from a Ladenburg flask into a wide-mouthed stoppered bottle kept in cold water, the cork being fitted with a calcium chloride tube. The distillate, a heavy colourless liquid, soon solidified to a white crystalline mass (flat hexagonal plates). The melting point was 56·7—56·8°.[1] The residue in the distilling flask was brown in colour.

(*d*) *Ethyl trichloracetate.*—This was prepared by Brühl's method [2] by keeping overnight a mixture of trichloracetic acid with eight to ten times the calculated quantity of absolute ethyl alcohol saturated with dry hydrogen chloride. The mixture was poured into water and the ester drawn off. It was then dried over fused calcium chloride

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[1] Sudborough and Lloyd, *J. Chem. Soc.*, 1899, **75**, 476.

[2] *Annalen*, 1880, **203**, 22.

and finally over anhydrous potassium carbonate, and carefully fractionated. The pure ester had a characteristic smell and boiled at 163—163·5° at 682 mm.

All the four substances when tested by means of a carefully standardized solution of sodium hydroxide gave a degree of purity of 99·5 to 100 per cent.

2. GENERAL PROCEDURE

The different substances were weighed out in as nearly equimolecular proportions as possible, and after thorough mixing (all the four substances were mutually soluble) were transferred to Jena hard glass bottles, which had been previously cleaned with concentrated hydrochloric acid, chromic acid mixture, and finally with distilled water, so as to be perfectly free from any traces of free alkali. The bottles were then placed in the thermostat at a temperature of 30°. The thermostat was a large water bath heated electrically and controlled by means of a regulator similar to the one described by Cumming.[1] The change of temperature of the thermostat was never greater than 0·02.

The amounts of free acid, ethyl acetate and ethyl trichloracetate present in the mixture were estimated at intervals of eight to ten days by removing three separate portions of the mixture by means of a 0·5 cc. pipette, weighing carefully and after solution in alcohol titrating as described on p. 3.

3. TESTING THE ACCURACY OF THE METHOD OF ESTIMATION

(*a*) A mixture containing 51·46 per cent. of trichloracetic acid and 48·54 per cent. of ethyl trichloracetate was used.

i. 1·103 gram required 24·27 cc. of 0·1432 N. ammonium hydroxide using methyl red as indicator = 51·45 per cent. of trichloracetic acid.

ii. 0·982 gram neutralized 21·61 cc. of the same alkali = 51·46 per cent. of the free acid.

iii. 1·125 gram neutralized 14·31 cc. of 0·4466 N. sodium hydroxide solution using phenolphthalein as indicator.

iv. 1·213 gram required 15·45 cc. of the same alkali. From iii and iv it follows that 1 gram of mixture would neutralize 0·2273 gram of sodium hydroxide when phenolphthalein is used as indicator and the difference

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[1] Trans. Faraday Soc., 1911, 7, 257. *Cf.* also this Journal, 1915, 1, 110; 1921, 4, 185.

between this and the alkali required in titrations i and iii (which gives the amount required for the free acid) is 0·1013 gram of sodium hydroxide which is equal to 48·43 per cent. of ethyl trichloracetate.

(*b*) A mixture containing 64·64 per cent. of acetic acid and 36·36 per cent. of ethyl acetate when analysed by the methods of titrations i and iii, given on p. 7, gave 64·7 per cent. of acetic acid and 35·3 per cent. of ethyl acetate.

(*c*) A mixture containing 54·3 per cent. of ethyl trichloracetate and 45·7 per cent. of ethyl acetate was taken.

A slight difficulty was met with in titrating the ethyl trichloracetate with standard sodium hydroxide in the presence of ethyl acetate and using phenolphthalein as indicator, as the pink colour is not permanent but disappears gradually owing to the slow saponification of the ethyl acetate. Repeated trials proved that the best results were obtained by taking the end point when the colour persisted for two minutes.

i. 1·238 gram neutralized 7·87 cc. of 0·4466 N. sodium hydroxide (= 0·1137 gram NaOH per gram of original mixture) using phenolphthalein as indicator, and equals 54·4 per cent. of ethyl trichloracetate.

ii. A second determination gave the same result.

iii. 1·227 gram of the mixture and 50 cc. of the standard sodium hydroxide solution were kept overnight and then titrated with 0·2548 N. hydrochloric acid. 48·92 cc. were required and, as this is equivalent to 27·91 of the alkali solution, the amount of alkali used for complete hydrolysis was 22·09 cc. or for 1 gram of mixture 0·3215 gram of sodium hydroxide. Deducting the amount required for the ethyl trichloracetate in 1 gram of the mixture, viz. 0·1137 (*cf.* i above) gives 0·2078 gram of sodium hydroxide required to hydrolize the ethyl acetate in 1 gram of mixture, i.e. 0·4572 gram of ethyl acetate or 45·7 per cent.

iv. A similar experiment also gave 45·7 per cent.

METHOD OF CALCULATION OF COMPOSITION OF EQUILIBRIUM MIXTURE

The original mixture contained 23·85 per cent. of acetic acid and 76·15 per cent. of ethyl trichloracetate.

Titration i.—0·652 gram in alcoholic solution required 18·10 cc. of 0·1434 N. ammonium hydroxide. One gram would therefore require 27·70 cc., which is equivalent to 0·1590 gram of sodium hydroxide and represents the amounts of free acids in 1 gram of the equilibrium mixture.

Titration ii.—An alcoholic solution of 0·5440 gram required 7·24 cc. of 0·4478 N. sodium hydroxide using phenolphthalein as indicator. One gram of mixture would require 13·31 cc. or 0·2384 gram of sodium hydroxide. The difference between this and the result of titration i, i.e. 0·2384 – 0·1590 = 0·0794 gram sodium hydroxide represents the amount of alkali used in saponifying the ethyl trichloracetate in the mixture = 0·3797 gram ethyl trichloracetate.

Titration iii. 0·5560 gram of the mixture was added to 20·0 cc. of 0·4478 N. sodium hydroxide and kept overnight and then required 17·75 cc. of 0·2560 N. hydrochloric acid for neutralization. The amount of alkali used up in neutralizing free acids and saponifying esters was therefore 9·85 cc. of 0·4478 N. solution. One gram of mixture would therefore require 17·71 cc. or 0·3181 gram of sodium hydroxide. The difference between this and titration ii, viz. 0·3181 – 0·2384 = 0·0797 gram sodium hydroxide, represents the amount of alkali required in saponifying the ethyl acetate in 1 gram of the mixture and is equal to 0·1754 gram of ethyl acetate.

As the amount of ethyl acetate was originally *nil*, 0·1188 gram of acetic acid must have been used up in producing this ethyl acetate and hence the amount of acetic acid present in 1 gram of the mixture at the time of titration was 0·2385 – 0·1188 = 0·1197 gram.

Similarly the amount of ethyl trichloracetate has diminished from 0·7615 to 0·3818 grams and must therefore have given rise to 0·3259 gram of free trichloracetic acid. The composition of the mixture is hence—

Acetic acid 11·88, ethyl acetate 17·54, trichloracetic acid 32·59, and ethyl trichloracetate 37·97 per cent.

The equilibrium constant can be calculated from the general formula

$$K = \frac{CH_3{\cdot}CO_2Et}{88{\cdot}1} \times \frac{CCl_3{\cdot}CO_2H}{163{\cdot}4} \div \frac{CH_3{\cdot}CO_2H}{60{\cdot}0} \times \frac{CCl_3{\cdot}CO_2Et}{191{\cdot}4}$$

where the formulæ represent the percentage of the substance present in the equilibrium mixture.

In the majority of cases the third titration was not made use of in calculating the composition of the equilibrium mixtures. From titrations i and ii, the amount of ethyl trichloracetate was calculated at equilibrium, the change in concentration of the ethyl trichloracetate entailed a corresponding alteration in the concentration of acetic acid, and an increase in the concentration of the ethyl trichloracetate entailed a corresponding decrease in the concentration of the trichloracetic acid and accompanying this would be a corresponding decrease in the concentration of the ethyl acetate.

The reaction took on an average two to three months to run to completion and it was considered to have attained equilibrium when two consecutive readings of Part II of the estimation (*cf.* p. 3) were practically the same. The amount of free acids determined by titration with standard ammonium hydroxide remains constant, since the amount of the one acid used up is equivalent to the other acid liberated from its ester. The amount of sodium hydroxide required for complete saponification of 1 gram of the mixture also remains constant.

EQUILIBRIUM CONSTANTS

The Tables 1—8 show the gradual change in the mixtures at various times. The actual calculations for the amounts of the four substances were only made when the mixture had attained equilibrium, and not at the time of each estimation.

The graphs obtained by plotting amount of change against time are similar to those given by Lichty[1] for the esterification of acids with an alcohol and by Lowry[2] and Küster[3] for cases of reversible isomeric change which attain an equilibrium.

In all these tables t = time in hours, a = grams of sodium hydroxide equivalent to the free acids in 1 gram of the mixture, b = grams of sodium hydroxide equivalent to the free acids *plus* ethyl trichloracetate and c = grams of sodium hydroxide required for complete neutralization and saponification of 1 gram of the mixture and is equivalent to the free acids *plus* ethyl trichloracetate *plus* ethyl acetate.

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[1] *Amer. Chem. J.*, 1896, **18**, 594.

[2] *J. Chem. Soc.*, 1899, **75**, 225.

[3] *Zeitsch. Physikal. Chem.*, 1895, **18**, 171.

TABLE I

A

Trichloracetic acid = 64·96 per cent.
Ethyl acetate = 35·04 do.
Molecular ratio 3·98 : 3·98

t	*a*	*b*	*c*
0	0·159	0·160	0·319
168	0·160	0·192	0·319
384	0·159	0·212	0·319
504	0·159	0·222	0·318
672	0·160	0·228	0·319
888	0·159	0·232	0·319
1008	0·159	0·236	0·318
1224	0·159	0·238	0·319
1416	0·159	0·239	0·319
1584	0·159	0·239	0·319

B

Trichloracetic acid = 65·20 per cent.
Ethyl acetate = 34·80 do.
Molecular ratio 4·00 : 3·96

t	*a*	*b*	*c*
0	0·160	0·160	0·318
336	0·160	0·197	0·318
648	0·160	0·211	0·318
936	0·160	0·233	0·318
1224	0·159	0·239	0·318
1512	0·160	0·239	0·318

At equilibrium the composition was therefore—

		A		B	
		Per cent.	Gram mols. per 1,000 grams	Per cent.	Gram mols. per 1,000 grams
Trichloracetic acid	=	32·27	1·98	32·93	2·02
Ethyl acetate	=	17·41	1·98	17·39	1·98
Acetic acid	=	12·01	2·00	11·85	1·97
Ethyl trichloracetate	=	38·28	2·00	37·80	1·98
K	=	**0·98**		**1·02**	

TABLE II

A

Acetic acid = 23·85 per cent.
Ethyl trichloracetate = 76·15 do.
Molecular ratio 3·98 : 3·98

t	*a*	*b*	*c*
0	0·159	0·318	0·318
168	0·159	0·286	0·318
336	0·160	0·263	0·318
504	0·160	0·255	0·318
672	0·160	0·247	0·317
840	0·160	0·244	0·317
1008	0·160	0·242	0·317
1176	0·159	0·240	0·318
1368	0·159	0·239	0·318
1560	0·159	0·238	0·318
1824	0·159	0·238	0·318

B

Acetic acid = 24·49 per cent.
Ethyl trichloracetate = 75·51 do.
Molecular ratio 4·08 : 3·95

t	*a*	*b*	*c*
0	0·163	0·321	0·321
240	0·163	0·282	0·321
528	0·163	0·266	0·321
816	0·163	0·253	0·321
1104	0·164	0·247	0·321
1680	0·163	0·241	0·322
1848	0·164	0·240	0·321
1944	0·163	0·240	0·321

At equilibrium the composition is—

		A		B	
		Per cent.	Gram mols. per 1,000 grams	Per cent.	Gram mols. per 1,000 grams
Trichloracetic acid	...	32·75	2·01	33·04	2·02
Ethyl acetate	...	17·66	2·01	17·79	2·02
Acetic acid	...	11·82	1·97	12·37	2·06
Ethyl trichloracetate	...	37·80	1·97	36·84	1·92
K	=	**1·03**		**1·03**	

TABLE III

A		B	
Ethyl acetate	= 28·24 per cent.	Ethyl acetate	= 28·04 per cent.
Acetic acid	= 19·28 do.	Acetic acid	= 19·39 do.
Trichloracetic acid	= 52·48 do.	Trichloracetic acid	= 52·57 do.
Molecular ratio	3·21 : 3·21 : 3·21	Molecular ratio	3·18 : 3·23 : 3·22
a	= 0·257	*a*	= 0·257
c	= 0·385	*c*	= 0·385

t	*b*	*t*	*b*
0	0·257	0	0·257
240	0·264	288	0·272
504	0·283	552	0·284
720	0·295	840	0·289
984	0·297	1152	0·293
1056	0·298	1440	0·297
1224	0·299	1776	0·299
2088	0·299	1968	0·299

At equilibrium the composition is therefore—

		A		B	
		Per cent.	Gram mols. per 1,000 grams	Per cent.	Gram mols. per 1,000 grams
Trichloracetic acid	...	35·33	2·16	35·41	2·17
Ethyl acetate	...	18·99	2·16	18·79	2·14
Acetic acid	...	25·48	4·25	25·69	4·28
Ethyl trichloracetate	...	20·10	1·05	20·10	1·05
K	=	1·04		1·03	

TABLE IV

A		B	
Ethyl acetate	= 26·85 per cent.	Ethyl acetate	= 25·66 per cent.
Acetic acid	= 18·55 do.	Acetic acid	= 17·76 do.
Ethyl trichloracetate	= 54·60 do.	Ethyl trichloracetate	= 56·58 do.
Molecular ratio	3·05 : 3·09 : 2·85	Molecular ratio	2·91 : 2·96 : 2·96
a	= 0·124	*a*	= 0·119
c	= 0·360	*c*	= 0·353

t	*b*	*t*	*b*
0	0·238	0	0·237
240	0·217	288	0·220
480	0·203	528	0·210
672	0·201	672	0·206
1824	0·199	960	0·203
2064	0·199	1248	0·201
		1872	0·198
		2136	0·198

At equilibrium the composition was—

		A		B	
		Per cent.	Gram mols. per 1,000 grams	Per cent.	Gram mols. per 1,000 grams
Trichloracetic acid	...	15·98	0·98	16·05	0·98
Ethyl acetate	...	35·49	4·03	34·31	3·90
Acetic acid	...	12·68	2·11	11·87	1·98
Ethyl trichloracetate	...	35·88	1·88	37·79	1·98
K	=	1·00		0·98	

TABLE V

A		B	
Ethyl trichloracetate	= 46·19 per cent.	Ethyl trichloracetate	= 45·87 per cent.
Acetic acid	= 14·55 do.	Acetic acid	= 14·58 do.
Trichloracetic acid	= 39·26 do.	Trichloracetic acid	= 39·55 do.
Molecular ratio	2·42 : 2·43 : 2·40	Molecular ratio	2·40 : 2·43 : 2·42
a	= 0·193	*a*	= 0·194
c	= 0·290	*c*	= 0·290

t	*b*	*t*	*b*
0	0·290	0	0·290
240	0·275	336	0·281
504	0·263	624	0·277
720	0·257	936	0·275
984	0·257	1800	0·263
1056	0·256	2160	0·257
2160	0·256	2520	0·257

At equilibrium the composition was—

		A		B	
		Per cent.	Gram mols. per 1,000 grams	Per cent.	Gram mols. per 1,000 grams
Trichloracetic acid	...	52·96	3·24	52·98	3·24
Ethyl acetate	...	7·39	0·84	7·24	0·82
Acetic acid	...	9·52	1·59	9·65	1·61
Ethyl trichloracetate	...	30·14	1·58	30·14	1·58
K	=		**1·09**		**1·04**

TABLE VI

A		B	
Ethyl acetate	= 19·89 per cent.	Ethyl acetate	= 19·50 per cent.
Ethyl trichloracetate	= 43·24 do.	Ethyl trichloracetate	= 43·84 do.
Trichloracetic acid	= 36·87 do.	Trichloracetic acid	= 36·67 do.
Molecular ratio	2·26 : 2·26 : 2·26	Molecular ratio	2·22 : 2·29 : 2·25
a	= 0·0903	*a*	= 0·0897
c	= 0·272	*c*	= 0·270

t	*b*	*t*	*b*
0	0·181	0	0·182
192	0·194	360	0·191
432	0·203	624	0·200
696	0·208	936	0·206
936	0·211	1272	0·208
1272	0·211	1560	0·211
1513	0·211	1896	0·211

At equilibrium the composition was—

		A		B	
		Per cent.	Gram mols. per 1,000 grams	Per cent.	Gram mols. per 1,000 grams
Trichloracetic acid	...	24·50	1·50	24·56	1·51
Ethyl acetate	...	13·22	1·50	12·97	1·48
Acetic acid	...	4·51	0·75	4·45	0·74
Ethyl trichloracetate	...	57·73	3·02	58·03	3·03
K	=		**0·99**		**1·01**

TABLE VII

A		B	
Acetic acid	= 11·67 per cent.	Acetic acid	= 13·58 per cent.
Ethyl acetate	= 17·52 do.	Ethyl acetate	= 24·38 do.
Trichloracetic acid	= 31·62 do.	Trichloracetic acid	= 19·12 do.
Ethyl trichloracetate	= 39·19 do.	Ethyl trichloracetate	= 42·92 do.
Molecular ratio	1·95 : 1·99 : 1·93 : 2·04	Molecular ratio	2·26 : 2·77 : 1·17 : 2·24
a	= 0·155	a	= 0·137
c	= 0·316	c	= 0·338

t	b	t	b
0	0·237	0	0·227
240	0·237	312	0·222
480	0·236	600	0·219
744	0·236	912	0·218
936	0·236	1248	0·218

At equilibrium the composition was—

		A		B	
		Per cent.	Gram mols. per 1,000 grams	Per cent.	Gram mols. per 1,000 grams
Trichloracetic acid	...	32·00	1·96	22·68	1·39
Ethyl acetate	...	17·72	2·01	26·30	2·99
Acetic acid	...	11·53	1·92	12·27	2·05
Ethyl trichloracetate	...	38·75	2·02	38·75	2·02
K	**=**		**1·01**		**1·02**

[Mean value of K from Tables I to VII = 1·02.]

VELOCITY CONSTANT

On p. 6 the equation

$$\frac{k}{V} = \frac{1}{2At} \ln \frac{A}{A - 2x}$$

has been deduced for the particular case where the initial concentrations of trichloracetic acid and ethyl acetate are represented by A gram molecules per 1,000 grams of mixture and the initial concentrations of acetic acid and ethyl trichloracetate are *nil* and $k_1 = k_2$. t denotes time in hours and x the number of gram molecules in 1,000 grams of mixture transformed in time t.

Substituting the original concentrations given in Table I-A., the equation becomes

$$\frac{k}{V} = \frac{1}{7{\cdot}96t}\left[\ln 3{\cdot}98 - \ln (3{\cdot}98 - 2x)\right]$$

$$= \frac{0{\cdot}289}{t}\left[\log 1{\cdot}99 - \log (1{\cdot}99 - x)\right]$$

$$= \frac{0{\cdot}289}{t}\left[0{\cdot}299 - \log (1{\cdot}99 - x)\right]$$

From Table I-A., the values of x can be calculated and the following values of $\frac{k}{V}$ have been obtained.

TABLE VIII

t	x	$0{\cdot}299-\log(1{\cdot}99-x)$	$\frac{k}{V}$
0	0	—	—
168	0·80	0·223	0·00038
384	1·30	0·460	0·00035
504	1·55	0·656	0·00038
672	1·70	0·837	0·00036
888	1·80	1·020	0·00033
1008	1·90	1·345	0·00039

Similarly the values of $\frac{k}{V}$ have been calculated from the data given in Table II-A. and are shown in Table IX.

TABLE IX

t	x	$0{\cdot}299-\log(1{\cdot}99-x)$	$\frac{k}{V}$
0	0	—	—
168	0·80	0·223	0·00038
336	1·38	0·514	0·00044
504	1·58	0·687	0·00039
672	1·78	0·977	0·00042
840	1·85	1·153	0·00040
1008	1·90	1·396	0·00040

With a mean value of $\frac{k}{V}$ for Tables VIII and IX of 0·00039.

II. The Equilibrium between Acetic Acid, Trichloracetic Acid and their Methyl Esters

The method adopted was exactly analogous to that described in Part I.

I. PREPARATION OF PURE SUBSTANCES

The acetic and trichloracetic acids were prepared by the methods indicated in Part I.

Methyl acetate.—This was prepared from methyl alcohol and acetic acid, using dry hydrogen chloride as the catalyst. It mixes in all proportions with water, and it is very difficult to effect a complete separation, as they form a constant boiling mixture. Calcium chloride was found to be useless as it forms an emulsion with the ester. Anhydrous potassium carbonate was found to be equally inefficient in removing the last traces of moisture. Phosphorus pentoxide was then used, as recommended by Young and Thomas[1] and by Perkin.[2] The ester was kept overnight over a large quantity of the phosphorus pentoxide which was transformed into a sticky jelly-like mass. After two distillations the pure ester, b.p. 53·5 at 680 mm. was obtained. The boiling point calculated from Young and Thomas's data (*loc. cit.*) upon the boiling point of methyl acetate at various pressures, and the vapour pressures at various temperatures respectively, is 53·5 and 53·7. When estimated by keeping a weighed quantity of the ester with excess of standard sodium hydroxide for fifteen to twenty hours, and then titrating the excess with hydrochloric acid, it was found to be 99·9 per cent. pure.

Methyl trichloracetate.—This was prepared by boiling a 5 per cent. solution of hydrogen chloride in methyl alcohol (8—10 molecules) with trichloracetic acid (1 molecule) for five hours. The ester separates on pouring into water and is drawn off. It is dried over anhydrous potassium carbonate and distilled. The pure ester boils at 150—150·5° under 679 mm. pressure. When estimated by dissolving a weighed quantity in alcohol and titrating with standard sodium hydroxide, it was found to be 99·9 per cent. pure.

2. TESTING METHOD OF ESTIMATION

The method of estimating methyl trichloracetate and methyl acetate in mixtures was similar to that described on p. 7.

The following numbers show that the method gives a fair degree of accuracy :—

1. 0·3840 gram of methyl trichloracetate required 19·1 cc. of 0·1120 N. sodium hydroxide solution, which is equivalent to 0·3800 gram of the ester.

2 A mixture containing 0·425 gram of methyl trichloracetate and 0·354 gram of ethyl acetate took 21·45 cc. of 0·1120 N. alkali for the first titration and 36·4 cc. of the same alkali for the subsequent titration. These numbers correspond with 0·426 gram of methyl trichloracetate and 0·358 gram of ethyl acetate.

3. A similar mixture containing 0·616 gram of methyl trichloracetate and 0·262 gram of ethyl acetate titrated in the same manner required 30·9 cc. and 23·2 cc. of 0·1120 N. alkali corresponding with 0·614 gram of methyl trichloracetate and 0·264 gram of ethyl acetate.

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[1] *J. Chem. Soc.*, 1893, **63**, 1194.

[2] *Ibid.*, 1884, **45**, 492.

3. EQUILIBRIUM CONSTANT

The values found for the titrations and the composition of the equilibrium mixtures are given in Tables X and XI.

TABLE X

	A	B
Trichloracetic acid	= 68·99 per cent.	= 69·13 per cent.
Methyl acetate	= 31·01 do.	= 30·87 do.
Molecular ratio	4·22 : 4·19	4·23 : 4·19
a	= 0·169	= 0·169
c	= 0·337	= 0·337

A t	A b	B t	B b
0	0·169	0	0·169
288	0·186	864	0·210
600	0·198	1920	0·237
864	0·209	3648	0·250
1104	0·216	3936	0·253
1344	0·222	4224	0·253
1632	0·228	4512	0·253
1920	0·233		
2496	0·242		
3072	0·249		
3648	0·253		
3888	0·253		
4128	0·253		

At equilibrium the composition was—

	A Per cent.	A Gram mols. per 1,000 grams	B Per cent.	B Gram mols. per 1,000 grams
Trichloracetic acid[1]	= 34·67	2·12	34·80	2·13
Methyl acetate	= 15·45	2·09	15·32	2·07
Acetic acid	= 12·60	2·10	12·60	2·10
Methyl trichloracetate	= 37·26	2·10	37·26	2·10
K	=	**1·00**		**1·00**

---

[1] The molecular weights used for calculation were respectively 163·4, 74·1, 60 and 177·4.

TABLE XI

Methyl trichloracetate = 74·53 per cent.
Acetic acid = 26·47 do.
Molecular ratio 4·20 : 4·25
a = 0·170
c = 0·338

t	b
0	0·338
312	0·320
648	0·303
984	0·289
1248	0·282
1824	0·270
2304	0·263
2880	0·258
3168	0·256
3456	0·254
3696	0·254
3936	0·254

At equilibrium the composition is—

		Per cent.	Gram mols. per 1,000 grams
Trichloracetic acid	...	34·32	2·10
Methyl acetate	...	15·56	2·10
Acetic acid	...	12·86	2·14
Methyl trichloracetate	...	37·27	2·10
K	=	**0·98**	

4. VELOCITY CONSTANT

Taking the equation on p. 6 and substituting the value for A given in Table X-A., where the molecular concentrations of the trichloracetic acid are taken as being equal, viz. 4·205 gram molecules per 1000 grams of mixture, the values of x given in Table XII have been calculated and from these the values of k/V.

TABLE XII

t	x	$0{\cdot}322 - \log\ (2{\cdot}10 - x)$	k/V.
0	0	—	—
288	0·425	0·098	0·000093
600	0·725	0·184	0·000084
864	1·00	0·281	0·000089
1104	1·18	0·354	0·000088
1344	1·32	0·430	0·000088
1632	1·48	0·530	0·000089
1920	1·60	0·623	0·000089

Similarly values for x have been calculated from the data given in Table XI for the reverse reaction. In this case the initial concentrations of the two substances are not quite the same and the value 4·225 has been taken as A. The values for x and k/V are given in Table XIII.

TABLE XIII

t	x	$3{\cdot}3243 - \log\ (2{\cdot}11 - x)$	$k/V.$
0	0	—	—
312	0·45	0·104	0·000091
648	0·875	0·233	0·000098
984	1·225	0·377	0·000104
1248	1·400	0·473	0·000103
1824	1·700	0·712	0·000106
2304	1·875	0·953	0·000112
2880	2·000	1·283	0·000121

With a mean value of k/V for Tables XII and XIII = **0·000097.**

SUMMARY AND GENERAL CONCLUSIONS

1. A method has been devised for ascertaining the amounts of free acids, ethyl trichloracetate and ethyl acetate in mixtures of the acids and esters.

2. It has been shown that the equilibrium constants of the two reactions—

$$CH_3{\cdot}CO_2Et \times CCl_3{\cdot}CO_2H \rightleftharpoons CH_3{\cdot}CO_2H \times CCl_3{\cdot}CO_2Et$$

and $CH_3{\cdot}CO_2Me \times CCl_3{\cdot}CO_2H \leftrightharpoons CH_3{\cdot}CO_2H + CCl_3{\cdot}CO_2Me$

are practically unity, although the relative strengths of the two acids vary considerably.

3. It follows that the relative affinities of ethoxy for acetyl, $CH_3{\cdot}CO$, and trichloracetyl $CCl_3{\cdot}CO$ are practically identical.

4. In the absence of a catalyst the reactions—

$$CH_3{\cdot}CO_2Et \times CCl_3{\cdot}CO_2H \longrightarrow CH_3{\cdot}CO_2H \times CCl_3{\cdot}CO_2\ Et$$
$$CCl_3{\cdot}CO_2Et \times CH_3{\cdot}CO_2H \longrightarrow CCl_3{\cdot}CO_2H \times CH_3{\cdot}CO_2\ Et$$

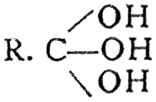
proceed slowly at 30° and at practically the same rates. The time required for the attainment of equilibrium is about 1,200—1,400 hours and if the equilibrium constant is taken as unity, then the two velocity constants are equal and the value of k/V at 30° is 0·00039.

Similarly with the methyl esters the equilibrium constant is practically unity and the two velocity constants at 30° have a value $k/V = 0{\cdot}000097$. The reaction is thus much slower in the case of acidolysis with methyl esters than with ethyl esters.[1]

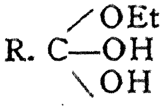
---

[1] The units used in calculating are time in hours, concentration in gram molecules per 1,000 grams and V = volume of 1,000 grams.

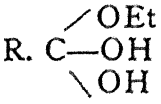
5. It is frequently assumed that in the processes of esterification, hydrolysis and alcoholysis intermediate additive compounds are formed. These additive compounds are regarded as derivatives of the ortho-acid.



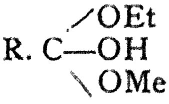
In esterification the intermediate product is formed from the acid and alcohol and may be represented as



In hydrolysis the additive compound[1] is derived from the ester and water

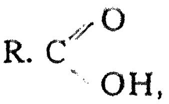


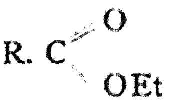
and splits up into alcohol and acid, and in alcoholysis the ester and a second alcohol (methyl) form an additive compound



which decomposes into methyl ester and ethyl alcohol.

It is possible that acidolysis is preceded by the formation of an additive compound of acid and ester,





Such additive compounds have actually been isolated, particularly those containing trichloracetic as one component.[2]

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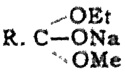
[1] A strong argument in favour of the formation of such additive compounds was Claisen's claim to the isolation of definite compounds of the type

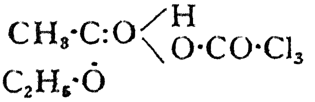


by the addition of sodium alkyl oxide to an ester. (*Ber.*, 1887, **20**, 646.) According to Tischenko (*J. pr. Chem.*, 1912, [11], **86**, 322), the products obtained by Claisen are not definite compounds but mixtures of alkali salts of the acids with some alcoholate. (Compare also Highley, *Amer. Chem. J.*, 1907, **37**, 394.)

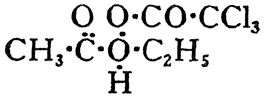
[2] J. Kendall and J. E. Booge, J. *Amer. Chem. Soc.*, 1916, **38**, 1712.

It is suggested by Kendall and Booge that the compounds may be of either type (*a*) or (*b*).

(*a*)



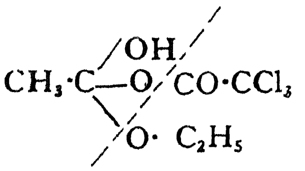
(*b*)



$$\mathrm{CH_3\cdot\overset{O}{\ddot{C}}\cdot\underset{H}{\overset{O\cdot CO\cdot CCl_3}{\dot{O}}}\cdot C_2H_5}$$

in which one of the oxygen atoms [in (*a*) the carbonyl oxygen and in (*b*) the ether oxygen] becomes quadravalent.

Such compounds are not analogous to those supposed to be formed during esterification, hydrolysis or alcoholysis. A compound of the ortho acid type formed from ethyl acetate and trichloracetic acid would be



and decomposition as indicated by the dotted line would give acetic acid and ethyl trichloracetate. Whether such intermediate compounds are formed is not known.

It is hoped to continue the investigation by an examination of the distribution of alcohol between a saturated acid and its $\alpha\beta$ unsaturated analogue, using both methyl and ethyl alcohols and further to determine the velocities of the processes of acidolysis in these cases.

In conclusion we have to thank Dr. H. E. Watson for valuable suggestions during the course of the work.

The Department of General and Organic Chemistry,
Indian Institute of Science,
Bangalore.