STUDIES IN ALCOHOLYSIS IV.

The alcoholysis of esters of $\alpha\beta$-unsaturated acids and of the corresponding saturated esters.

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INTRODUCTION.

In previous communications attention has been drawn to the close relationships between the processes of esterification, alcoholysis and hydrolysis of esters. Kolhatkar (This Journal, 1915, *1*, 127 and J. Chem. Soc. 1915, *107*, 921), as the results of determining the velocity constants of alcoholysis of various esters of saturated fatty acids by the dilatometric method, was able to show that, for the following acids, *viz.*, formic, acetic, propionic, *n*-butyric, trichloracetic and benzoic, the relative rates of esterification by the catalytic method and of alcoholysis of the corresponding ethyl esters by means of hydrogen chloride follow the same order. Kolhatkar was also able to show that the ratio of the constants for reactions of Ethyl ester $\longrightarrow$ Methyl ester and Methyl ester $\longrightarrow$ Ethyl ester is practically the same for acetates, propionates and butyrates, in other words, that the relative affinities of the ethyl and methyl groups towards an acyl radicle are to a large extent independent of the nature of the acyl group, a conclusion which has also been drawn by Hemptinne (Zeitsch. physikal. Chem., 1894, *13*, 562) Lowenherz (*ibid*, 1894, *15*, 389) and J Meyer (*ibid.*, 1909, *66*, 81) by a study of the hydrolysis of the methyl, ethyl, propyl and butyl esters of various acids by means of dilute hydrochloric acid.

Sudborough, N. B. Bhagvat and V. K. Bhagvat (This Journal, 1918, *2*, 121) have drawn attention to the fact that, in the absence of a catalyst, esters of strong acids undergo alcoholysis more readily than the esters of weak acids, just as by the process of direct esterification strong acids are esterified more rapidly than weak acids; and finally Sudborough and Karvé (This Journal, 1919, *3*. 1) have shown that two ortho substituents in the acyl portion of an aromatic ester are able completely to inhibit alcoholysis when either sodium alkyl oxides or mineral acids are used as catalysts, just as these substituents inhibit esterification

(V. Meyer and Sudborough, Ber., 1894, *27*, 510, 1580, 3146) by the catalytic process or hydrolysis of aromatic esters by mineral acids (V. Meyer, Ber., 1895, *28*, 188).

According to Sudborough and Roberts (Journ. Chem. Soc., 1905, *87*, 1842) Sudborough and E. R. Thomas, (*ibid.*, 1907, *91*, 1033), Sudborough and Gittins (*ibid.*, 1909, *95*, 315) an acid containing an *αβ*- unsaturated linking is esterified far more slowly than its saturated analogue when the catalytic method of esterification is used, and T. Williams and Sudborough (*ibid.*, 1912, *101*, 412) have shown that the ethyl esters of *αβ*- unsaturated acids are hydrolysed much more slowly than the esters of the corresponding saturated acids.

As the processes of catalytic esterification and alcoholysis under the catalytic influence of hydrogen chloride have been shown to be similar in so many respects, we desired to ascertain whether an *αβ*- unsaturated linking in the acyl portion of an ester has a pronounced retarding effect on alcoholysis using hydrogen chloride as catalyst.

With this object in view we have carried out two series of determinations of the velocity constants of alcoholysis of esters of *αβ*- unsaturated acids and of the esters of the corresponding saturated acids.

In the one series of experiments we have used a dilatometric method very similar to that used by Kolhatkar (*loc cit.*) and in the other series we have adopted a polarimetric method.

The present paper gives a description of the results of the first series of experiments; the results of the second series will be given later.

For the dilatometric experiments the following series of reactions were selected.

1. Methyl butyrate + ethyl alcohol ⟶ Ethyl butyrate + methyl alcohol.
2. Methyl crotonate + ethyl alcohol ⟶ Ethyl crotonate + methyl alcohol.
3. Methyl hydrocinnamate + ethyl alcohol ⟶ Ethyl hydrocinnamate + methyl alcohol.
4. Methyl cinnamate + ethyl alcohol ⟶ Ethyl cinnamate + methyl alcohol.

and the corresponding reverse reactions.

Experimental.

Preparation of esters and purification of alcohols.

These were prepared by the Fischer-Speier method of esterification or by the action of alkyl iodides on the silver salts of the acids using benzene as diluent.

With the exception of methyl cinnamate, which is a solid, the esters were purified by fractional distillation, occasionally under reduced pressure. The methyl cinnamate was purified by crystallisation from methyl alcohol in which it is readily soluble.

Table I gives the boiling or melting points of the esters used.

The alcohols used were Kahlbaum's 99·8 per cent ethyl alcohol and his acetone free methyl alcohol. These were finally dehydrated by treating several times with fresh calcium turnings and redistillation into a receiver provided with a calcium chloride tube—about 2·5 grams of calcium per litre of alcohol was used each time.

The methyl alcohol so dehydrated had a density $D_4^{25}=$ 0·78687. (corrected to a vacuum) as compared with the value $D_4^{25}=0·78658$ (corrected) given by Klason and Norlin (Arkiv Kem. Min. Geol., 1906, *2*, No. 24, 1.)

The ethyl alcohol had a value $D_4^{25}=0·78534$. (corrected to a vacuum) as compared with the values 0·78506 (cor.) given by Osborne and Bearce (American Bureau of Standards, 1913, *9*, 435.) and the value 0·78509 (cor.) given by Klason and Norlin (*loc. cit*).

Preparation of mixtures for filling the dilatometers.

The alcoholic solution of hydrogen chloride was prepared in the usual manner, taking care to exclude atmospheric moisture, and was made about twice the concentration required for the actual experiments. A solution of the ester in the requisite alcohol was made such that the concentration was roughly 10 molecules of alcohol to 1 of ester and equal volumes of the hydrogen chloride and ester solutions were mixed and the mixture used for filling the dilatometers.

The dilatometers.

These were not of quite the same shape as those used by Kolhatkar. The actual shape is given in Diagram 1. a. The bulb A

TABLE I.

Ester.	Boiling point (cor.) at p mm.	Corrected pressure p in mm.	Boiling point at 760.	Reference.	
				Boiling point at 760	Authority.
Methyl butyrate ...	98·3—99·2	679	102·4—3·3 b.	102·8	Otto Schumann Ann. Phys. Chem. 1882, *12*, 48.
Ethyl butyrate ...	115--116	681	119—120	119·9	
Methyl crotonate ...	115—116	680·5	118·6—119·6	120·7 (a)	Kahlbaum. Ber., 1879, *12*, 344.
Ethyl crotonate ...	133—134	682	136·7—137·7	142—3 (a)	Kramer and Gredzki. Ber., 1878, *11*, 1359.
				138·6	Bruhl. Annalen, 1886, *235*, 9.
Methyl hydrocinnamate ...	230	680·5	234·3	236·6 (a)	Weger. Annalen, 1883, *221*, 78.
Ethyl hydrocinnamate ...	242—243	680	246·5—247·5	248·1 (a)	Weger. Annalen, 1883, *221*. 78.
				245·8—246·1	Bruhl. Annalen, 1879, *200*, 192.
Ethyl cinnamate ...	167	40	271 (appx.)	271 (a)	Anschutz and Kinnicut, Ber., 1878, *11*, 1220.

Methyl cinnamate : Melting point 33·5°C as compared with 33·4°C given by Anschutz and Kinnicut, Ber., 1878, *11*, 1220.

(a) It is not stated whether any correction has been applied or not to these readings.

(b) The values in this column were obtained by using the relationship between increments in b. p. due to an increase of 10 mm. pressure between 700 and 760 mm. given by Von Rechenberg (Gewinnung and Trennung der Aetherischen Oele p. 497) for liquids with practically the same boiling points.

has a capacity of 31 c c., the capillary a capacity of 0·002. c.c. per centimetre, and the portion BC a length of 40-45 cms. The stem is bent at B and C, so that a number of dilatometers may be supported in the thermostat by the same clamps, one near B and the other near C. The stems of all dilatometers can be kept in contact without either bulbs or cocks interfering, as they would if the whole capillary were straight. Thus as many as nine dilatometers (see Diagram 2) can be easily supported and observations of the movement of liquid in the capillaries of all these can be made with a single cathetometer. The bulb A is pear shaped and not spherical. If the whole of the liquid in the stem, which is kept vertical, flows back into the bulb owing to an accidental fall of temperature, then with such a bulb the liquid will rise again into the capillary without leaving an air space when the temperature is restored. A spherical bulb would, under similar circumstances, tend to form a dead air space as shown in Diagram 1 (c). The object of the small reservoir at D is to trap the liquid, if by a short accidental rise in temperature its volume increases to such an extent that, without the reservoir, the liquid might be forced against the cock and a small amount lost.

The small reservoir is also of assistance in filling the bulb with the mixture to the desired height. The liquid is introduced into the bulb in the ordinary manner by evacuation, care being taken that a slight excess enters. To remove the excess, the dilatometer is cooled so that the liquid passes from the stem to the bulb and air enters; by tilting the dilatometer, a small column of liquid corresponding with the surplus to be removed enters the stem whilst a bubble of air remains in the bulb; then by gently warming with the hand the liquid above the air is made to enter the reservoir D and can then be removed by tilting the dilatometer, the open end F being lower than C Diagram 1 (b) andconnected to a pump. The cock E is then closed, the dilatometer disconnected from the pump and the cock carefully opened.

The cock of each dilatometer was lubricated with a trace of a mixture prepared from bee's wax, shellac and turpentine and when the bulbs had been filled the open capillary end was closed by means of a pin and beeswax. Each time before a reading of the meniscus was taken, the cock was opened and the pin removed to adjust the pressure inside with that outside.

The Thermostat.

The thermostat was similar to the one described by Kolhatkar (*loc. cit.* p. 110); the only change introduced consisted in having an automatic arrangement, by means of which, when the voltage of the mains supplying the current to the heating bulbs was insufficient to maintain the temperature at 30°, one or even two extra lamps were introduced into the heating circuit. The current was admitted through an iron lever, one side of which acted as an armature to an electro-magnet which was connected to the mains through about 600 ohms resistance. On the other side weights were so placed that if the voltage in the mains approached the critical value referred to above, the end with the weights descended making contact and thus supplying current to the extra lamps.

Reading the meniscus.

The total change for complete alcoholysis corresponds with about 100 mm rise or fall of the meniscus in the capillary stem of the bulb. The reading miroscope used was provided with a vernier reading to 0·1 mm., and was capable of rotation about its vertical axis, so that the position of the meniscus in each of the dilatometers could be easily read.

Causes of change in the position of the meniscus.

The alteration in the position of the meniscus in the stem of the dilatometer may be due to the following causes:—

(a) Slight alteration in the temperature of the thermostat.

(b) Direct action of the hydrogen chloride on the alcohol giving rise to an alkyl chloride and water. At 30°C this reaction cannot be neglected as already shown by Kolhatkar (*loc. cit.*, p. 115).

This reaction produces an increase in the volume of the reacting mass and hence a rise of the meniscus in the capillary.

The change is much more rapid in the case of methyl than with ethyl alcohol.

(c) Direct action of the hydrogen chloride on the ester. So far as is known no such action occurs and this source of error has been neglected.

(d) The process of alcoholysis resulting in the exchange of alkyl groups.

As the object of the research was to study the change due to (d) only, in order to obtain accurate results it was necessary to eliminate the changes in volume due to (a) and (b). This was accomplished by introducing into the thermostat a second dilatometer of the same shape and size as the first and containing an alcoholic solution of hydrogen chloride of the same strength as that used for studying the process of alcoholysis. Whenever a reading of the meniscus of the dilatometer, in which alcoholysis was proceeding, was made, a reading of the meniscus of the second dilatometer was also taken and as the changes due to (a) and (b) would be the same in both, the difference between the changes of the two meniscuses was taken as the measure of the amount of alcoholysis occuring in the first dilatometer.

If 5 or 6 experiments were being conducted at the same time using the same alcohol, only one dilatometer containing a solution of hydrogen chloride in the given alcohol was necessary for the control of the experiments.

As the dilatometers themselves, although supported by the clamps might have their positions accidentally altered, a fixed mark was etched on each stem and the position of the mark checked before a reading was made.

Calculation of the Velocity Constant.

In all the experiments a large excess of alcohol was used, roughly 20 molecules of alcohol to one of ester, and under such conditions the reaction

$$R{\cdot}COOR' + R''{\cdot}OH \rightleftharpoons R{\cdot}COOR'' + R'{\cdot}OH.$$

should become practically unimolecular and hence the constant can be calculated by means of the usual equation for a unimolecular reaction, *viz.*

$$k = \frac{1}{t} \ln \frac{a}{a-x} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

Kolhatkar used this equation for calculating the constants and determined the value of a, *i. e.*, the alteration for 100 per cent. change, by allowing the reaction to proceed until no further alteration in the position of the meniscus occurred. This method takes up much time and also the end point is difficult to determine.

We have modified the formula (1) with the object of eliminating the determination of the final end point.

The ordinary equation (1) for a unimolecular reaction may be written as

$$\frac{a-x}{a} = e^{-kt}$$

Differentiating with respect to t, it becomes

$$\frac{dx}{dt} = a\,k\,e^{-kt}$$

If x_1, x_2, x_3, etc. are values of x at times t_1, t_2, t_3, etc., then $X_{2,1}$ the rate of change at time $T_{2,1}$, which is the mean between t_1 and t_2, may be written approximately as $\frac{x_2-x_1}{t_2-t_1}$.

Thus

$$X_{2,1} = \frac{x_2-x_1}{t_2-t_1} = a\,k\,e^{-k\,T_{2,1}} \;;$$

similarly

$$X_{3,2} = a\,k\,e^{-k\,T_{3,2}}$$

hence

$$\frac{X_{2,1}}{X_{3,2}} = e^{k(T_{3,2}-T_{2,1})}$$

$$\text{or} \qquad k = \frac{1}{T_{3,2}-T_{2,1}} \ \text{ln.}\ \frac{X_{2,1}}{X_{3,2}}$$

In this way the values of k may be calculated from pairs of adjacent readings and the mean value taken. We have prepared, however, to plot the logarithms of $X_{2,1}$, $X_{3,2}$, etc. against times $T_{2,1}$, $T_{3,2}$, etc. The points should all lie on a straight line and its inclination to the time axis is the diminution in unit time of the logarithm of the rate of change, which is k. Some typical graphs are reproduced in Diagrams III to VI.

As the value of k is directly proportional to the concentration of the catalyst (Kolhatkar *loc cit*. p. 117) in all our experiments the values of k have been calculated for 0·02N hydrogen chloride.

EXPERIMENTAL RESULTS.

In the tables given under reactions I to VIII the actual experimental data are given. In these tables the following abbreviations are adopted.

D=Date on which the experiment was started.

R=Ratio of molecules of alcohol to ester in the solution containing alcohol, ester and catalyst.

C=Concentration of the hydrogen chloride.

e =Reading in mm. of the meniscus in the dilatometer containing the mixture of alcohol, ester and catalyst.

c =Reading in mm. of the meniscus in the dilatometer containing the alcohol and catalyst.

e–c=x.

t = Time in minutes in reactions I, III, V and VII and in the rest it is in hours.

T=Mean time between any two consecutive readings of *t* or two readings not too far apart.

l =Logarithm to the base 10 of the rate of change.

k=Velocity constant at 30°C for a concentration 0·02N of hydrogen chloride, and the minute being taken as the unit of time throughout.

Const.=Value of k when common logarithms are used and a concentration of catalyst 0·02N.

Table II gives a list of the values of *k* at 30° for the eight reactions studied.

Reaction I. Methyl Butyrate+Ethyl Alcohol.

(1) D=30—9—19 R=20·9 C=0·0808·N.

t	e	c	e—c =x	Change in x	Change in t	T	l
0	41·5	20·5	21·0	...	...	...	...
210	60·0	21·1	38·9	17·9	210	105	$\bar{2}$·930
870	91·2	25·8	65·4	26·5	660	540	$\bar{2}$·605
2400	102·3	26·5	75·8	12·0	1530	1630	$\bar{3}$·895

Const.$=169\times10^{-6}$

(2). D=20—11—19 R=20·6 C=0·0442·N.

0	7·4	4·6	2·8	...	...	...	...
200	19·1	3·3	15·8	13·0	200	100	$\bar{2}$·815
540	35·2	4·7	30·5	14·7	340	370	$\bar{2}$·636
1160	52·0	5·3	46·7	16·2	620	850	$\bar{2}$·420
1500	56·0	5·5	50·5	...	...	...	...
1980	67·6	7·0	60·6	13·9	820	1570	$\bar{2}$·230
2640	71·5	6·5	65·0	14·5	1140	2070	$\bar{2}$·105
3480	76·5	8·5	68·0	7·4	1500	2730	$\bar{3}$·695

Const.$=167\times10^{-6}$

Contd.—Reaction I. Methyl Butyrate+Ethyl Alcohol.

(3) D= 6—12—19 R=23·0 C=0·0335

t	e	c	e—c =x	Change in x	Change in t	T	1
0	12·2	7·7	4·5	...	...	...	...
220	20·3	8·4	11·9	7·4	220	110	$\bar{2}$·525
480	27·7	8·8	18·9	7·0	260	350	$\bar{2}$·430
1170	41·0	9·2	31·8	12·9	690	820	$\bar{2}$·270
1810	48·1	7·4	40·7	8·9	640	1490	$\bar{2}$·135
2830	57·4	9·0	48·4	7·7	1020	2320	$\bar{3}$·88
4570	63·2	9·7	53·5	12·8	1740	3700	$\bar{3}$·467

Const $=170\times10^{-6}$

N. B.—Anhydrous calcium chloride was added to the ester, allowed to stand for 2 days to be quite sure that the low values of k·02 are not due to moisture in the ester. The ester distilled fractionally and the following experiment carried out.

(4) D=29 9·20 R=15·6 C=0·03698·N.

0	6·8	4·3	2·5	...	...	...	...
65	11·0	5·0	6·0	3·5	65	32	$\bar{2}$·630
390	22·5	2·3	20·2	14·2	325	227	$\bar{2}$·540
1055	48·0	3·4	44·6	24·4	665	722	$\bar{2}$·465
1366	55·2	3·6	51·6	7·0	311	1210	$\bar{2}$·250
1546	61·0	5·8	55·2	3·6	180	1456	$\bar{2}$·200
1816	66·4	6·6	59·7	4·5	270	1680	$\bar{2}$·120
2692	75·8	7·8	68·0	8·3	876	2255	$\bar{3}$·875
2981	76·6	6·75	69·85	1·85	289	2837	$\bar{3}$·705

Const. $=180\times10^{-6}$

$$k = 396{\cdot}0\times10^{-6}$$

Reaction II. Methyl Crotonate + Ethyl Alcohol.

(1) D=26—2—20. R=18·4. C=·0908·N.

t	e	c	e-c=x	Change in x	Change in t.	T	l
0	6·6	4·8	1·8				
24	20·7	7·8	12·9				
49	29·5	7·0	22·5	20·7	49	24·5	$\bar{1}$·625
73·5	44·7	10·8	33·9	21·0	49·5	49·0	$\bar{1}$·627
98	49·8	10·1	39·7	17·2	49·0	73·0	$\bar{1}$·545
118	55·7	11·4	44·3				
146	61·8	12·4	49·4	15·5	72·5	110	$\bar{1}$·330
166	67·5	14·3	53·2	13·5	68	132	$\bar{1}$·300
190	72·1	15·5	56·6	12·3	72	154	$\bar{1}$·235
214	72·7	14·0	58·7				
238	75·9	14·5	61·4	12·0	92	192	$\bar{1}$·115
262	78·3	15·1	63·2	10·0	96	214	$\bar{1}$·020
312	82·7	17·5	65·2	8·6	122	251	$\bar{2}$·850
377	81·6	13·2	68·4	5·2	262	320	$\bar{2}$·655

Const. $=12\cdot4\times10^{-6}$

(2) D=16—3—20. R=25. C=0·09285.

0	5·0	1·5	3·5				
23·5	16·2	5·1	11·1				
48	24·6	6·4	18·2	14·7	48	24	$\bar{1}$·485
72·5	29·6	5·6	24·0	12·9	49·0	36	$\bar{1}$·420
94·5	32·3	3·8	28·5	10·3	46·5	71	$\bar{1}$·345
144	43·3	8·4	34·9	10·9	71·5	108	$\bar{1}$·185
168	46·4	10·0	36·4	7·9	73·5	131	$\bar{1}$·030
192	49·2	10·3	38·9	4·0	48	168	$\bar{2}$·920
216	50·1	10·0	40·1	3·7	48	192	$\bar{2}$·887
260	55·5	13·2	42·3	3·4	68	226	$\bar{2}$·70
312	59·7	15·3	44·4	4·3	96	264	$\bar{2}$·65
360	63·2	17·5	45·7	3·4	100	310	$\bar{2}$·53

Const. $=12\cdot9\times10^{-6}$

$k=29\cdot0\times10^{-6}$

Reaction III. Methyl Hydrocinnamate + Ethyl Alcohol.

(1) D=20—11—19. R=20. C=0·0422·N.

t	e	c	e-c=x	Change in x	Change in t	T	l
0	22·6	4·6	18·0				
150	27·7	3·3	24·4				
270	33·8	3·2	30·6	12·6	270	135	$\bar{2}$·67
500	45·3	4·7	40·6	10·	230	380	$\bar{2}$·65
1120	63·8	5·3	58·5	17·9	620	810	$\bar{2}$·46
1470	70·4	5·5	64·9				
1930	79·1	7·0	72·1	18·6	810	1520	$\bar{2}$·225
2600	84·5	6·7	77·8	12·9	1130	2030	$\bar{2}$·057
3420	90·6	8·5	82·1	10·0	1490	2670	$\bar{3}$·827
4680	93·0	8·5	84·5	12·4	2750	3300	$\bar{3}$·655

Const. = 165 × 10^{-6}

(2) D=6—12—19. R=20·4. C=0·0323·N.

0	11·5	7·7	3·8				
120	18·4	8·0	10·4				
240	23·2	8·4	14·8	11·0	240	120	$\bar{2}$·66
500	33·5	8·8	24·7	9·9	260	370	$\bar{2}$·58
1140	50·3	9·2	41·1	16·4	640	820	$\bar{2}$·41
1830	59·7	7·4	52·3	11·2	690	1485	$\bar{2}$·21
2850	72·5	9·0	63·5	11·2	1020	2340	$\bar{2}$·04

Const. = 165 × 10^{-6}

$k = 382{\cdot}0 \times 10^{-6}$

Reaction IV. Methyl Cinnamate+Ethyl Alcohol.

(1) D=26—2—20. R=21·4. C=0·08722N.

t	e	c	e-c =x	Change in x	Change in t	T	l
0	6·5	4·8	1·7	...	...	...	...
24	15·1	7·8	7·3	...	...	...	...
49	19·6	6·2	13·4	11·7	49	24·5	$\bar{1}$·378
73·5	31·6	10·8	20·8	13·5	49·5	49	$\bar{1}$·435
98	35·2	10·1	25·1	11·7	49·	73·5	$\bar{1}$·378
118	39·1	10·0	29·1	8·3	44·5	96·0	$\bar{1}$·27
146	45·4	12·4	33·0	...	...	...	...
166	50·8	14·4	36·4	11·3	68	132	$\bar{1}$·22
190	55·3	15·4	39·9	10·8	72	154	$\bar{1}$·175
214	56·5	14·3	42·2	9·2	68	180	$\bar{1}$·130
286	64·5	16·4	48·1	8·2	96	238	$\bar{2}$·93
377	67·7	13·2	54·5	6·4	91	331·5	$\bar{2}$·85

Const· $8{\cdot}95 \times 10^{-6}$

(2) D=16—3—20. R=21·6. C=0·08896N.

0	8·5	1·5	7·0	...	...	...	...
24	19·8	5·1	14·7	...	...	...	...
48	28·3	6·4	21·9	14·9	48	24	$\bar{1}$·490
72·5	33·9	5·6	28·3	13·6	48·5	48	$\bar{1}$·450
93·5	38·5	3·8	34·7	12·8	45·5	71	$\bar{1}$·45
144	52·7	8·4	44·3	9·6	50·5	119	$\bar{1}$·28
168	58·3	10·0	48·3	...	...	...	...
192	61·9	10·3	51·6	7·3	48	168	$\bar{1}$·18
216	64·1	10·0	54·1	5·8	48	192	$\bar{1}$·08
260	70·8	13·2	57·6	6·0	68	226	$\bar{2}$·945
312	77·3	15·3	62·0	7·9	96	264	$\bar{2}$915
360	82·1	17·5	64·6	7·0	100	310	$\bar{2}$·845
				2·6	48	336	$\bar{2}$·735

Const·$=9{\cdot}7 \times 10^{-6}$

$k=21{\cdot}5 \times 10^{-6}$

Reaction V. Ethyl Butyrate+Methyl Alcohol.

(1) D=13—1—20. R=20. C=0·0167·N.

t	e	c	e-c = x	Change in x	Change in t	T	l
0	106·6	28·1	78·5	...	...	...	...
30	104	28	76·	...	...	...	...
50	99·7	27·5	72·2	6·3	50	25	$\bar{1}$·1
95	94·4	27·5	66·9	9·1	65	62	$\bar{1}$·145
155	86	26·5	59·5	12·7	100	100	$\bar{1}$·105
285	71	25·5	45·5	14·0	130	220	$\bar{1}$·032
360	65	26	39	6·5	75	322	$\bar{2}$·94
600	54	30·3	23·7	15·3	240	480	$\bar{2}$·805
1260	31	32·5	—1·6	25·2	660	930	$\bar{2}$·582
2640	18·5	30·7	—12·2	10·6	1380	1940	$\bar{3}$·89

Const. 778×10^{-6}

(2) D=26—3—20. R=20. C=0·01875·N.

0	112·2	4·1	108·1	...	...	...	...
55	105·7	4·8	100·9	...	...	...	...
130	96·4	4·8	91·6	16·5	130	65	$\bar{1}$·105
255	87·1	5·0	82·1	18·8	200	155	$\bar{2}$·975
515	71·5	5·6	65·9	16·2	260	385	$\bar{2}$·795
1170	55·6	7·7	47·9	18·0	660	840	$\bar{2}$·435
1500	50·4	6·6	43·8	4·1	330	1330	$\bar{2}$·195

Const.= 786×10^{-6}

N. B.—Anhydrous calcium chloride was added to the ester, allowed to stand for 2 days to be quite sure that the low values of k·02 are not due to moisture in the ester. The ester distilled fractionally and the following experiments carried out.

(3) D=29—9—20. R=28. C=0·01262·N.

0	103·4	39·4	64·0	...	...	...	...
65	98·4	39·7	58·7	5·3	65	32	$\bar{2}$·910
390	71·8	35	36·8	21·9	325	225	$\bar{2}$·828
1055	44·2	36	8·2	28·6	665	720	$\bar{2}$·635
1366	37·5	36·1	1·4	6·8	310	1210	$\bar{2}$·340
1816	34·4	39·35	—4·95	6·85	450	1590	$\bar{2}$·150
2692	27·8	39·65	—11·85	6·9	876	2255	$\bar{3}$·896

Const.= 780×10^{-6}

$k = 1805 \times 10^{-6}$

Reaction VI. Ethyl Crotonate+Methyl Alcohol.

(1) D=13—1—20. R=20. C=0·0171·N.

t	e	o	e-o = x	Change in x	Change in t	T	l
2·6	104	26·5	77·5	...	...	...	...
21·0	99·3	32·5	66·8	10·7	18·4	11·8	$\bar{1}$·765
44·	87·5	30·7	56·8	10·0	23	32·5	$\bar{1}$·637
71	79·0	32·5	46·5	10·3	27	57·5	$\bar{1}$·580
142	59·0	32·0	27·0	19·5	71	106·5	$\bar{1}$·44
168	51·0	30·2	20·8	...	...	...	...
192	45·5	28·8	16·7	10·3	50	167	$\bar{1}$·315
216	42·5	30·0	12·5	8·3	48·	192	$\bar{1}$·237

Const. = $52{\cdot}2 \times 10^{-6}$

(2) D=16—3—20. R=21·8. C=0·02806·N.

0	102·4	3·4	99·0	...	...	...	...
24	82·9	6·4	76·5	22·5	24	12	$\bar{1}$·972
48	66·5	6·7	59·8	16·7	24	36	$\bar{1}$·842
72	52·1	6·0	46·1	13·7	24	60	$\bar{1}$·755
93	39·3	3·8	35·5	10·6	21	82	$\bar{1}$·702
144	28·6	8·7	19·9	15·6	51	118	$\bar{1}$·485
168	24·6	9·7	14·9	...	...	...	...
192	21·7	10·3	11·4	8·5	48	168	$\bar{1}$·248
216	17·9	9·9	8·0	6·9	48	192	$\bar{1}$·157
260	17·1	12·8	4·3	7·1	68	226	$\bar{1}$·020
312	17·2	15·4	1·8	6·2	96	264	$\bar{2}$·810
360	17·9	17·9	0	4·3	100	310	$\bar{2}$·630

Const. = $55{\cdot}3 \times 10^{-6}$

Reaction VI.—*Contd.* Ethyl Crotonate+Methyl Alcohol.

(3). D=19—5—20. R=23·2. C=0·02629·N.

t	e	e	e-e x	Change in x	Change in t	T	l
4·5	97·2	6·1	91·1	...	...	...	...
28	82·7	6·9	75·8	15·3	23·5	16·2	$\bar{1}$·814
49	70·2	7·2	63·0	12·8	21·0	38·5	$\bar{1}$·785
78·5	65·3	14·6	50·7	12·3	29·5	63·7	$\bar{1}$·620
101	54·4	11·3	43·1	7·6	22·5	89·7	$\bar{1}$·53
125	53·5	15·8	37·7	5·4	24	113	$\bar{1}$·352
149	45·4	12·6	32·8	4·9	24	137	$\bar{1}$·310
189	42·2	14·5	27·7	5·1	40	169	$\bar{1}$·105
262	39·8	17·6	22·2	5·5	73	225	$\bar{2}$·877
365	38·3	19·9	18·4	3·4	103	313·5	$\bar{2}$·519

Const.—$56{\cdot}0 \times 10^{-6}$

$k = 125 \times 10^{-6}$

Reaction VII. Ethyl Hydrocinnamate+Methyl Alcohol.

(1) D=13—1—20. R=21·7. C=0·01622·N.

t	e	c	e-c=x	Change in x	Chage in t	T	l
0	103	28·1	74·9	...	...	...	...
30	101	28·0	73·0	...	...	...	...
50	97·6	27·5	70·1	...	...	...	...
95	94	27·5	66·5	8·4	95	47	$\bar{2}$·945
155	88	26·5	61·5	11·5	125	92	$\bar{2}$·965
285	77·0	25·0	52·0	14·5	190	190	$\bar{2}$·882
360	72·5	26·0	46·5	15·0	205	257	$\bar{2}$·865
575	65·2	30·3	34·9	11·6	215	467	$\bar{2}$·732
1260	47·0	32·5	14·5	20·4	690	920	$\bar{2}$·47
2640	33	30·7	2·3	12·2	1380	1950	$\bar{3}$·945

Const.=672×10^{-6}

(2) D=26—3—20. R=34·0. C=0·01942·N.

t	e	c	e-c=x	Change in x	Chage in t	T	l
0	97·4	4·1	93·3	...	...	...	...
55	93·2	4·8	88·4	...	...	...	...
130	86·5	4·8	81·7	11·6	130	65	$\bar{2}$·95
255	79·8	5·0	74·8	13·6	200	155	$\bar{2}$·832
515	69·4	5·6	63·8	11·0	260	385	$\bar{2}$·625
1170	57·3	7·7	49·6	14·2	655	840	$\bar{2}$·335
1500	53·1	6·6	46·5	3·1	330	1330	$\bar{3}$·973
2730	49·8	7·3	42·5	4·0	1230	2110	$\bar{3}$·512

Const.=676×10^{-6}

$k = 1560 \times 10^{-6}$

Reaction VIII. Ethyl Cinnamate + Methyl Alcohol.

(1) D=16—3—20. R=20. C=0·0265·N.

t	e	o	e-o =x	Change in x	Change in t	T	l
0	82·2	3·4	78·8	...	...	...	...
24	74·1	6·4	67·7	11·1	24	12	$\bar{1}$·665
48	64·1	6·7	57·4	10·3	24	36	$\bar{1}$·632
72	53·6	6·0	47·6	9·8	24	60	$\bar{1}$·611
93	43·5	3·8	39·7	7·9	21	82·5	$\bar{1}$·575
144	34·6	8·7	25·9	13·8	51	118·5	$\bar{1}$·432
168	30·2	9·7	20·5	...	...	...	...
192	26·5	10·3	16·2	9·7	48	168	$\bar{1}$·305
216	22·7	9·9	12·8	7·7	48	192	$\bar{1}$·205
260	19·6	12·8	6·8	9·4	68	226	$\bar{1}$·14
312	16·5	15·4	1·1	11·7	96	264	$\bar{1}$·085
360	16·4	17·9	—1·1	8·3	100	310	$\bar{2}$·92

Const.$=34·5\times10^{-6}$

(2) D=19—5—20. R=21·5. C=0·02509·N.

4·5	103·6	6·1	97·5	...	...	...	...
28	93·6	6·9	86·7	10·8	23·5	16·2	$\bar{1}$·662
49	83·1	7·2	75·9	10·8	21	38·5	$\bar{1}$·710
78·5	78·4	14·6	63·8	12·1	29·5	63·7	$\bar{1}$·613
101	68·5	11·3	57·2	6·6	22·5	89·7	$\bar{1}$·467
125	67·2	15·8	51·4	5·8	24	113	$\bar{1}$·383
149	59·0	12·6	46·4	5·0	24·0	137	$\bar{1}$·318
189	54·1	14·5	39·6	6·8	40	169	$\bar{1}$·23
214	50·6	14·4	36·2	3·4	25	201·5	$\bar{1}$·135
237	49·4	15·8	33·6	...	...	...	...
262	48·0	17·6	30·4	5·8	48	238	$\bar{1}$·082
285	44·5	16·7	27·8	5·8	48	261	$\bar{1}$·082
311	42·6	17·3	25·3	5·1	49	287	$\bar{1}$·020
337	44·3	20·9	23·4	4·4	52	311	$\bar{2}$·93
365	41·7	19·9	21·8	3·5	5·4	338	$\bar{2}$·812
405	40·4	21·3	19·1	4·3	68	371	$\bar{2}$·80
437	38·7	21·3	17·4	4·4	72	401	$\bar{2}$·785
485	43	21·9	21·1	...	...	...	...
549	44·4	25·3	19·1	2·0	64	517	$\bar{2}$·495

Const.$=33·2\times10^{-6}$

$k=78·0\times10^{-6}$

TABLE II.

Mixture.	K × 10^6 at 30°C for 0·02 N HCl. for alcoholysis.	K for Hydrolysis for N· HCl at 20°†	K for Esterification for N HCl.
I. Methyl Butyrate + Ethyl Alcohol	396		50·0*
II. Methyl Crotonate + Ethyl Alcohol	29		1·28*
III. Methyl Hydrocinnamate + Ethyl Alcohol ...	382		47·3*
IV. Methyl Cinnamate + Ethyl Alcohol	21·5		0·937*
V. Ethyl Butyrate + Methyl Alcohol	1805	0·0657	
VI. Ethyl Crotonate + Methyl Alcohol	125	0·00225	
VII. Ethyl Hydrocinnamate + Methyl Alcohol ...	1560	0·0201	15·4‡
VIII. Ethyl Cinnamate + Methyl Alcohol	78·0	0·000672	0·43‡

N. B,—The unit of time in alcoholysis constant is the minute, while in esterification and hydrolysis it is the hour. Kailan's values were obtained at 25°C while those of Sudborough and Roberts at 15°C. Again Kailan's values for esterification here given viz. 15·4 and 0·43 were obtained by multiplying the values given by him, by 2·3016, in order to convert K given by him from calculations based on ordinary logarithms, to the Naperian logarithms.

*Sudborough and Roberts. J. C. S. 1909, *95*, 315.

†Sudborough and Williams. J. C. S. 1912, *101*, 412.

‡Anton Kailan, Monatsh., 1907, *28*, 1143, 1153.

DISCUSSION OF RESULTS.

The values of k for the reactions :—

(1) Methyl butyrate + ethyl alcohol → Ethyl butyrate
+ methyl alcohol

and (2) Ethyl butyrate + methyl alcohol → Methyl butyrate
+ ethyl alcohol

do not agree with those obtained by Kolhatkar (*loc. cit.* p. 126). The values for the densities of the alcohols used (p. 183) compared with the values for the absolute alcohols indicate the presence of small amounts of water, practically 0·1 per cent.

According to Anton Kailan (Monatsh., 1907, *28*, 1137) the quantitative relationships between the percentage diminution of the rates of esterification and the amount of water present (when the amounts are small) are practically independent of the acid and alcohol employed. If the same generalisation holds good for alcoholysis, then, taking Kohlhatkar's values (*loc. cit.* p. 128) for the effect of water on the alcoholysis of ethyl acetate with methyl alcohol and assuming that our low value for the alcoholysis of ethyl butyrate with methyl alcohol is due to the influence of water, then the presence of 0·05 per cent of water in the methyl alcohol is indicated. In the case of methyl butyrate and ethyl alcohol, the presence of 0·16 per cent of water is indicated.

II. A glance at the values given in table II shows that the esters containing an $\alpha\beta$- olefinic linking in the acyl group undergo alcoholysis far less readily than the esters of the corresponding saturated acids. Thus

	Alcohol	Esterification.	Hydrolysis.
$\frac{\text{K methyl butyrate}}{\text{K methyl crotonate}}$	= 13·6	39·0	—
$\frac{\text{K methyl hydrocinnamate}}{\text{K methyl cinnamate}}$	= 17·8	50·5	—
$\frac{\text{K ethyl butyrate}}{\text{K ethyl crotonate}}$	= 14·5	—	29
$\frac{\text{K ethyl hydrocinnamate}}{\text{K ethyl cinnamate}}$	= 20·0	36·0	30

The results indicate that the ratio is of the same order of magnitude in the four cases and that the mean value is 16·5.

Although the $\alpha\beta$- linking has a marked retarding effect upon alcoholysis, this effect is not so great as in esterification, where the mean value for 3 pairs of acids is 42, as compared with a value 29·5 for hydrolysis of the esters with dilute hydrochloric acid.

III. A further comparison of the alcoholysis constants given in table II shows that the rate is decreased by replacing a β-methyl group by phenyl.

The actual values are :—

	Alcoholysis.	Esterification.	Hydrolysis
$\frac{\text{K methyl butyrate}}{\text{K methyl hydrocinamate}}$	$= \frac{396}{382}$	1·1 †	—
$\frac{\text{K methyl crotonate}}{\text{K methyl cinnamate}}$	$= \frac{29}{21·5}$	1·4 †	—
$\frac{\text{K ethyl butyrate}}{\text{K ethyl hydrocinnamate}}$	$= \frac{1805}{1560}$	—	3·3*
$\frac{\text{K ethyl crotonate}}{\text{K ethyl cinnamate}}$	$= \frac{125}{78·0}$	—	3·35*

IV. The results also confirm Kolhatkar's generalisation that in the case of alcoholysis, the ratio of the constants for the direct and the reverse reactions is roughly independent of the nature of the acyl group.

The actual values are :—

Ratio of the constants of alcoholysis for methyl to ethyl and ethyl to methyl.

		$\frac{\text{K ethyl ester.}}{\text{K methyl ester.}}$
Butyrates ...	...	4·6
Crotonates ...	...	4·4
Hydrocinamates	...	4·1
Cinnamates ...	...	3·6
	Mean	4·2

as compared with Kolhatkar's value (*loc. cit.* p. 130) of 3·7

In conclusion we have to thank Dr. H. E. Watson for several valuable suggestions in connection with the work.

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I. I. S. No. 78—R. P. B.—4-1921—500.

Diagram I.

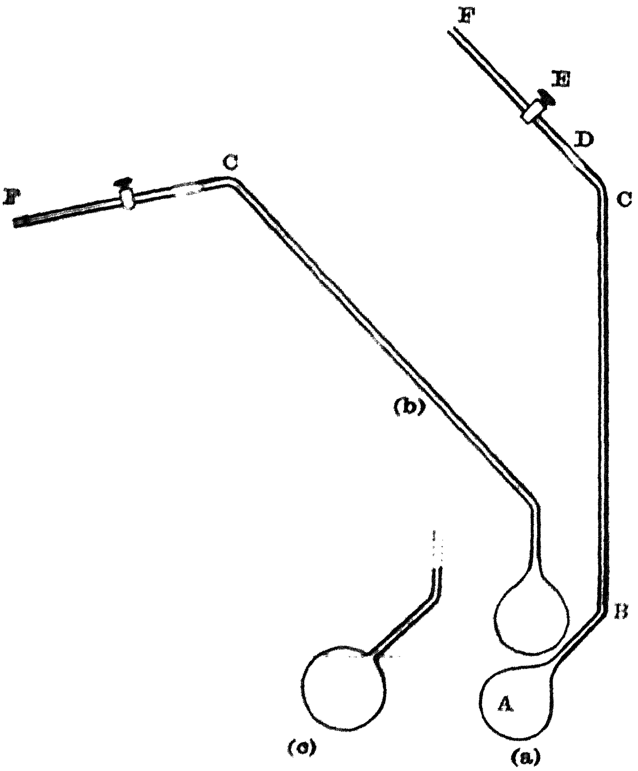


Diagram II.

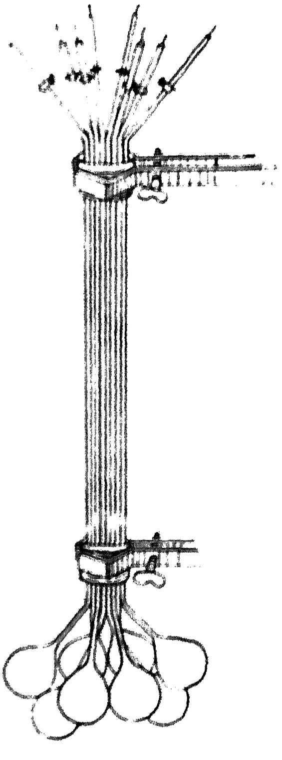
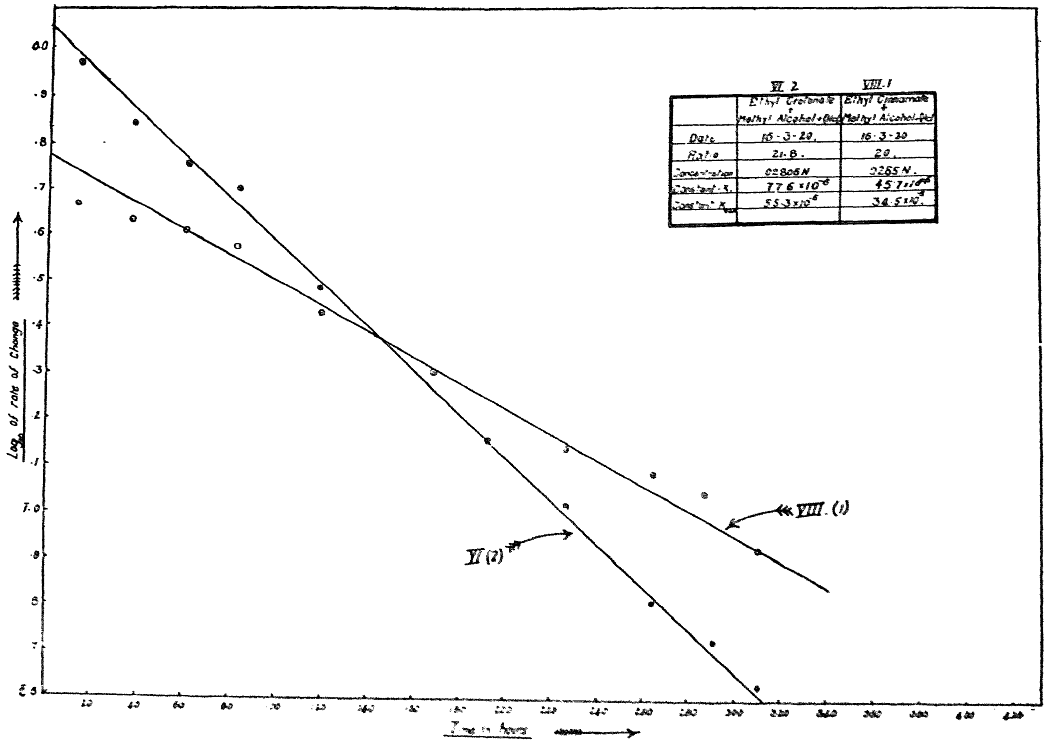
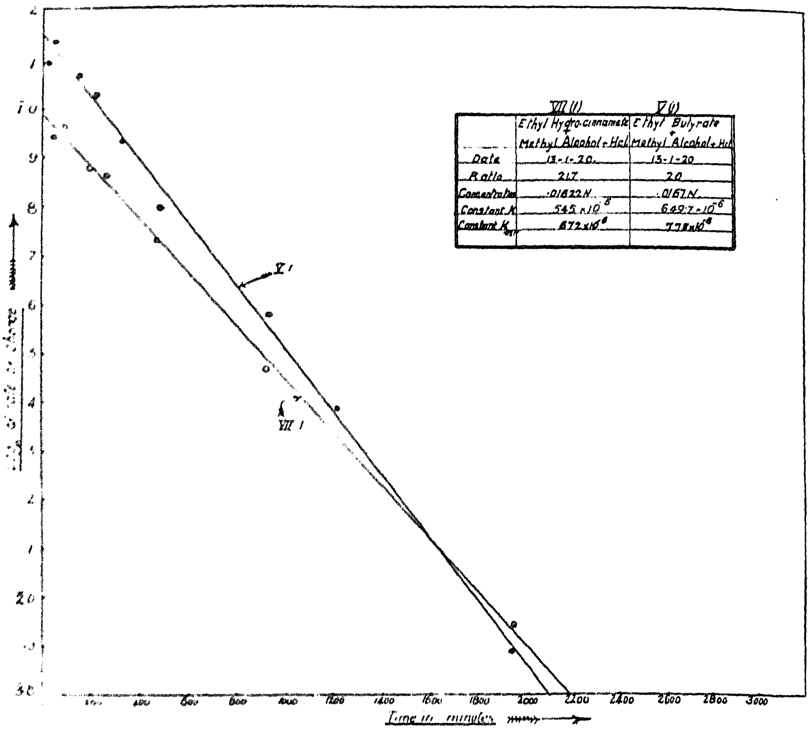


Diagram IV.



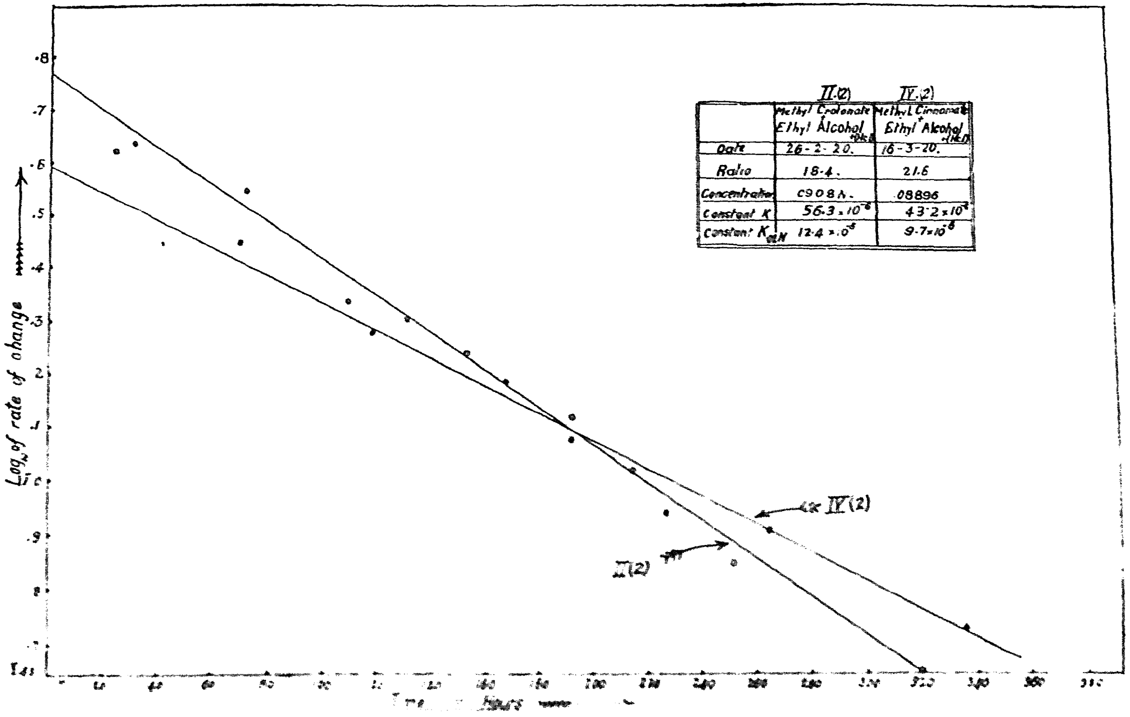
	VI. 2	VIII. 1
	Ethyl Crotonate + Methyl Alcohol + [illegible]	Ethyl Cinnamate + Methyl Alcohol-[illegible]
Date	16-3-20.	16-3-30
Ratio	21·8.	20.
Concentration	·02806 N	·0265 N.
Constant K.	77.6×10^{-6}	45.7×10^{-6}
Constant $K_{[illegible]}$	55.3×10^{-6}	34.5×10^{-6}.

Diagram V.



	VII (1)	V (1)
	Ethyl Hydro-cinnamate + Methyl Alcohol + Hcl	Ethyl Butyrate + Methyl Alcohol + Hcl
Date	13-1-20.	13-1-20
Ratio	21.7	20
Concentration	·01822 N.	·0167 N.
Constant K	545×10^{-8}	$649 \cdot 7 \times 10^{-6}$
Constant K	672×10^{-6}	778×10^{-6}

Diagram VI.



	II·(2) Methyl Crotonate + Ethyl Alcohol +HCl	IV·(2) Methyl Cinnamate + Ethyl Alcohol +HCl
Date	26-2-20.	16-3-20.
Ratio	18·4.	21·6
Concentration	·0908 N.	·08896
Constant K	$56{\cdot}3 \times 10^{-6}$	$43{\cdot}2 \times 10^{-6}$
Constant $K_{\alpha N}$	$12{\cdot}4 \times 10^{-6}$	$9{\cdot}7 \times 10^{-6}$