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CONTENTS.

STUDIES IN ALCOHOLYSIS. V.

The Alcoholysis of Esters of $\alpha\beta$-unsaturated Acids and of the corresponding saturated Esters.

BY

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The Alcoholysis of Esters of $\alpha\beta$-unsaturated Acids and of the corresponding saturated Esters.

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I. INTRODUCTION.

In a previous communication[1] results were given of the alcoholysis of ethyl and methyl esters of crotonic and cinnamic acids, *i.e.* having a double linkage of carbon atoms in the $\alpha\beta$-position to the carboxyl, and also of their corresponding saturated analogues, with large excess of nearly absolute methyl or ethyl alcohol, respectively. These reactions were carried out at 30°C in the presence of dry hydrogen chloride as catalyst. In all cases the velocity constants were proportional to the strength of the catalyst in the reacting mixture, and these constants were tabulated for 0·02 N. catalyst. As was expected from analogous reactions, *viz.* the hydrolysis of these esters, and esterification of the corresponding acids, the double linkage of the $\alpha\beta$-carbon atoms exert a marked retarding influence on the alcoholysis. In esterification the ratios of the constants of the saturated to unsaturated compound is 42 : 1, in hydrolysis 30 : 1 and in alcoholysis 16·5 : 1.[2] The replacement of the β-methyl group by phenyl slightly decreases the velocity constant. The ratio of the constants for the direct and the reverse reaction is the same for butyrate, crotonate, hydrocinnamate and cinnamate, as was also found by Kolhatkar[3] for acetates, propionates, and butyrates, although the ratios differ to some extent, as one of the reacting alcohols contained traces of water.

In what follows, an account is given of further examples of alcoholysis at 30° in presence of excess of alcohol with dry hydrogen chloride as catalyst, and embracing the following series of reactions with optically active esters :—

I. Menthyl butyrate + Methyl alcohol⟶
Methyl butyrate + Menthol.

II. Menthyl crotonate + Methyl alcohol⟶
Methyl crotonate + Menthol.

III. Menthyl hydrocinnamate + Methyl alcohol⟶
Methyl hydrocinnamate + Menthol.

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[1] B. Dasannacharya and J. J. Sudborough. *This Journal*, 1921, 4, 181.

[2] *loc. cit.*, p. 202.

[3] G. B. Kolhatkar. *This Journal*, 1915, 1, 130.

IV. Menthyl cinnamate + Methyl alcohol⟶
Methyl cinnamate + Menthol.

V. Methyl butyrate + Menthol⟶
Menthyl butyrate + Methyl alcohol.

VI. Methyl crotonate + Menthol⟶
Menthyl crotonate + Methyl alcohol.

VII. Ethyl butyrate + Menthol⟶
Menthyl butyrate + Ethyl alcohol.

The velocity constant in each case was calculated from the observed change in optical rotation of the reacting mixture, corrections being applied for diminution of the velocity constant owing to a fall in the strength of the catalyst during the reaction, and also for a diminution of the optical rotation of the mixture owing to the direct action of the catalyst, when menthol was used as the reacting alcohol. In all cases velocity constants were calculated for normal strength of catalyst.

The polarimetric method has been previously used for studying the alcoholysis of esters with an optically active alcohol. Thus Bruni and Contardi [1] examined the reaction between molecular quantities of menthol and the following esters at 100° in the absence of a catalyst:—ethyl acetate, aceto-acetate, oxalate, malonate and benzoate.

Jessie Elizabeth Minor [2] also used the polarimetric method to study the equilibrium concentrations when menthyl aceto-acetate is treated with a series of aliphatic alcohols and found that they vary only within fairly narrow limits at the high temperature used, showing that the relative affinities of the various alcohol-alkyls for the hydroxyl and acyl group are about the same. It was also pointed out that in an alcoholysis reaction where the alkyl radicles in the ester and alcohol are of similar constitution the equilibrium should not be far from 50 per cent provided equimolecular quantities react. The paper contains a critical survey of previous work and a list of the literature on alcoholysis.

II. EXPERIMENTAL

A. *Preparation and Purification of the Esters and Alcohols*

(*a*) *Methyl esters.*—The methyl esters of butyric and crotonic acids and ethyl butyrate were prepared by the Fischer-Speier method,

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[1] Bruni and Contardi, *Atti R. Accad. Lincei*, 1906, [v.] 15, 637; *Gazzetta*, 1906, 36, 356.
[2] Dissertation: Bryn Mawr College, 1917.

or by the action of alkyl iodides with the silver salts of the acids, using benzene as diluent. Purification was effected by fractional distillation.

Methyl butyrate: b.p. 679 = 98·3 − 99·2
or b.p. 760 = 102·4 − 103·3
(b.p. 760 = 102·8 Otto Schumann[1]).
Ethyl butyrate: b.p. 681 = 115 − 116°
or b.p. 760 = 119 − 120°
(b.p. 760 = 119·9° Otto Schumann[1]).
Methyl crotonate, b.p. 680·5 = 115 − 116°
or b.p. 760 = 118·6 − 119·6°
(b.p. 760 = 120·7° Kahlbaum[2]).

(*b*) *Menthyl esters.*—The method was the same as was employed by Rupe and his collaborators.[3] A perfectly clear benzene solution of the acid chloride was added gradually to a solution of 1 gm. mol. of menthol and 1·5 mol. of pure pyridine in a little benzene.

The acid chloride, was prepared by the action of thionyl chloride on the acid. The reaction takes place in the cold or on slight warming. Sulphur dioxide and hydrogen chloride are liberated and the acid chloride distilled off. The thionyl chloride (Kahlbaum's) used boiled at 72·73° under 670·5 mm. pressure.

The properties of the menthyl esters used are given in Table I.

TABLE I.

Menthyl esters.

——	Boiling point	Pressure in mm.	Density	Optical rotation $[\alpha]_D$
Menthyl butyrate ...	115·0 − 115·8	8·3	0·9038 at 30° 0·9049 at 26·6°	− 69·53° without solvent at 28°
Menthyl crotonate ...	124—125°	9·5	0·9195 at 38·2°	− 84·53 at 25°. without solvent
			0·9289 at 25·2°	− 83·51 at 45°. without solvent
Menthyl hydrocinnamate	181—182°	5·0	...	− 56·5 at 30° in benzene solution.
Menthyl cinnamate ...	Not distilled as decomposes	...	...	− 76·8 at 30·8° in benzene solution.

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[1] *Ann. Phys. Chem.*, 1882, 12, 48.

[2] *Ber.*, 1879, 12, 344.

[3] *Annalen*, 1909, 369, 319.

These values agree fairly well with those given by Rupe[1] and Tschugaeff.[2]

(*c*) *Alcohols.*—Acetone-free methyl alcohol was repeatedly dehydrated with small amounts of metallic calcium till the distilled product did not alter in density on further treatment with calcium.

The density found at 25° was the same as that given by Klasson and Norlin,[3] viz. 0·78658 when reduced to a vacuum.

In the previous investigation a slightly higher value was obtained and the alcoholysis of ethyl butyrate with the methyl alcohol indicated 0·05 per cent of water, which might have been introduced by the catalyst not being thoroughly dried. It is feared that the same uncertainty exists as regards the present results. It is well, however, to state that this quantity could not be large as great care was taken to exclude water vapour. The gas was produced by the action of concentrated sulphuric acid on anhydrous sodium chloride. The gas was led through two wash bottles containing pure, concentrated sulphuric acid, before it was admitted into the alcohol. Atmospheric water vapour was excluded by using a calcium chloride tube. The alcohol and the alcoholic solution of the catalyst were always kept in a desiccator.

Menthol.—This was obtained from the British Drug Houses, Ltd., London, and was in the form of long white needles melting at 42·0°.

For the preparation of the esters this menthol was used without further purification. But for alcoholysis in reactions V, VI, VII, it was further purified by distillation under a pressure of about 10 mm.

The melting point, was unchanged, and the specific rotation in dry benzene was

$$[\alpha]^{28\cdot3}_{\mathrm{D}} = -47{\cdot}20$$

as compared with

$$\left.\begin{array}{l}[\alpha]^{20}_{\mathrm{D}} = -48{\cdot}96\\ [\alpha]^{40}_{\mathrm{D}} = -49{\cdot}55\end{array}\right\}\begin{array}{l}\text{without solvent}\\ \text{Pickard and Kenyon}^{4}\end{array}$$

$$\left.\begin{array}{l}[\alpha]^{18\cdot1}_{\mathrm{D}} = -49{\cdot}78\\ [\alpha]^{29\cdot7}_{\mathrm{D}} = -49{\cdot}95\end{array}\right\}\begin{array}{l}\text{in ethyl alcohol}\\ \text{Patterson and Taylor}^{5}\end{array}$$

The low value for the rotation makes it probable that distillation racemised a little of the menthol.

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[1] *Annalen*, 1909, **369**, 319.

[2] *J. Russ Phys. Chem. Soc.*, 1902, **34**, 606

[3] *Arkiv. Kem. Min. Geol.*, 1906, **2**, No. 24, 1.

[4] *J. Chem. Soc.*, 1915, **107**, 52.

[5] *Ibid.*, 1905, **87**, 130.

B. *Preparation of Mixtures for Alcoholysis.*

Hydrogen chloride prepared by the action of pure concentrated sulphuric acid was bubbled through bottles containing pure concentrated sulphuric acid and then into a flask containing the alcohol ; a little cotton-wool served to prevent acid spray from contaminating the alcohol. Contamination of the alcohol through atmospheric moisture was prevented by a calcium chloride tube. A mixture was also prepared of the alcohol and the requisite ester. Equal volumes of the two were mixed and placed in a two decimetre polarimeter tube. This was fixed horizontally below the surface of the water in an electrically heated, toluene-regulated thermostat, at 30°C. Both ends of the tube protruded from the thermostat, but this did not introduce any serious error as the temperature of the surrounding air was not far from that of the thermostat. The thermostat could be so moved that a polarimeter tube could be either brought between the nicols of the polarimeter or moved away, thus permitting an observation of the rotation of another tube without disturbing the thermostat.

Changes in optical rotation.

The alcoholysis was followed by observing the change in optical rotation of the mixture for yellow sodium light. This change would be exactly proportional to the amount of alcoholysis provided changes of rotation due to the direct action of the catalyst on the ester or on the products of alcoholysis were absent or compensated. No appreciable direct action was found in the case of alcoholysis I to IV with methyl alcohol for the concentration of the catalyst, up to 0·5 N.

In a mixture of menthol with 10 per cent of benzene and 0·6930 N hydrogen chloride the rotations given in Table II were observed in a 2-decimetre tube at 30°.

TABLE II.

Rotations of hydrogen chloride (0·6930 N.) and menthol at 30°.

Time in hours	Rotation in Degrees
0	79·63
30	79·61
70	79·60
140	79·62
215	79·61
310	79·61

These values show that there is no direct action of hydrogen chloride on menthol for the concentration of 0·6930 N.

Further, it has been shown that at the same temperature the change in strength of catalyst observed for thirty-five days is practically the same, for the following mixtures :—

(*a*) A half normal solution of hydrogen chloride in methyl alcohol.

(*b*) Methyl alcohol and hydrogen chloride as in (*a*) with addition of menthyl crotonate, the ratio of crotonate to alcohol being about the same as in the alcoholysis mixtures.

(*c*) Methyl alcohol and hydrogen chloride (same as in the above) with menthol, the same equivalent amount as the menthyl crotonate.

The results are given in Table III.

TABLE III.

No. of days from start	Titration Values in c.c. [1] of 0·5348 N. Sodium hydroxide for 2 c.c. of the solution		
	Experiment (*a*)	Experiment (*b*)	Experiment (*c*)
0	1·72	1·72	1·72
1	1·68	1·68	1·69
6	1·45	1·43	1·41
12	1·24	1·10	1·21
35	0·93	0·85	0·86

It is to be concluded therefore that the action of hydrogen chloride is on the optically inactive methyl alcohol and not to any appreciable extent on the menthyl ester or on the menthol.

If, however, the concentration of the catalyst is largely increased the direct action becomes pronounced. Table IV gives the rotation of two solutions of menthol with 10 per cent benzene, for 1·27 N. and 2·55 N. hydrogen chloride respectively.

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[1] Measured from a 10 c.c. standard burette reading to 0·02 c.c.

TABLE IV.

No. of days from start	Rotation in Degrees	
	1·27 N.	2·55 N.
1	−85·59	−87·84
8	85·59	87·62
11	...	87·56
14	85·56	87·49
39	85·36	86·73

This correction has to be allowed for, in calculating the rotation due to alcoholysis alone.

Strength of Catalyst.

Experiment I (1) (page 11) with menthyl butyrate, methyl alcohol and 0·02434 N. hydrogen chloride showed that the reaction was very slow so that in subsequent experiments, viz. I (2) and I (3), the concentration of the catalyst was increased 10 to 15 times. When, however, in Experiments II and IV it was found desirable to use still higher concentrations, owing to the reactions being very much slower, the direct action of hydrogen chloride on the methyl alcohol became pronounced and it was necessary to allow for this change, the extent of which is shown in Table III.

III. CALCULATION OF RESULTS.

The reactions studied have been of the following type :—

(1) A unimolecular alcoholysis reaction. The strength of the catalyst remains unchanged during the reaction as this proceeds rapidly. Reactions I and III are of this nature. Reaction VII, namely, Ethyl butyrate + Menthol⟶Menthyl butyrate + Ethyl alcohol, though slow, has the strength of catalyst remaining constant as the catalyst has practically no direct action on the menthol or on the ethyl alcohol formed during the course of the reaction.

(2) A unimolecular alcoholysis reaction together with an independent change in strength of catalyst brought about by the dire
action of the catalyst on the reacting alcohol, resulting in a gra
di[illegible] of the velocity constant. To this [illegible] . (b).

$$\frac{dx}{dt} = k\,(a-x)\,(C-y) \,.\,.\,.\,.\,.\,.\,.\,.\,.\,. (2).$$

(3) A unimolecular alcoholysis reaction together with a side reaction bringing about a change in strength of the catalyst proportional to the extent of the alcoholysis. For example, in reaction V, Methyl butyrate + Menthol⟶Menthyl butyrate + Methyl alcohol, the hydrogen chloride has no action on the menthol so long as its concentration is below 0·5 N.; but it acts strongly on the methyl alcohol formed in the reaction and thus brings about a continuous fall in the concentration of the catalyst and consequently a fall in the velocity constant.

(4) When the strength of catalyst exceeds 0·5 N., the hydrogen chloride begins to act on the menthol and produces a diminution in optical rotation of the mixture. As the diminution is small—0·026° in 100 hours—the correction can be simply added to the observed change of rotation of the mixture. Reaction VI is an example of this type.

For calculating the velocity constant in reactions of type (1) the formula derived in a previous paper [1] has been used.

$$k = \frac{1}{C} \frac{1}{T_{3,2} - T_{2,1}} \ln \frac{X_{2,1}}{X_{3,2}}$$

k is the velocity constant, $X_{2,1}$, $X_{3,2}$ . . . are rates of change at times $T_{2,1}$, $T_{3,2}$ . . . respectively of the ester or of any property of the solution, such as change of volume or change of optical rotation, which is proportional to the amount of ester that has changed. Logarithms of $X_{2,1}$, $X_{3,2}$ . . . , are plotted against $T_{2,1}$, $T_{3,2}$, . . . the line passing through the several points makes with the axis of time an angle whose tangent is k, corresponding with the strength of catalyst C. As k is directly proportional to the strength of catalyst, k corresponding with normal hydrogen chloride as catalyst has been calculated.

Reactions of the type (2).—Here the change in the strength of the catalyst is about 12 per cent depending on the time during which the reaction has been proceeding. As the change is independent of the main reaction, we can write,

$$\frac{dx}{dt} = k\,(a-x)\,(C-y) \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (2)$$

$$\frac{dy}{dt} = k'\,(C-y) \;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;.\;. \quad (3)$$

a = the amount of ester in the mixture, to start with.
C = concentration of the catalyst to start with.
x = change in the amount of ester at time t from start.
y = change in the strength of catalyst, at time t.
k and k' are constants.

Dividing (2) by (3),

$$\frac{dx}{dy} = (a-x)\,\frac{k}{k'}$$

$$-\frac{d\,(a-x)}{a-x} = dy\,\frac{k}{k'}$$

On integrating,

$$-\ln\,(a-x) = y\,\frac{k}{k'} + \text{a constant} \quad . \; . \; . \quad (4)$$

when $x=0$, $y=0$, the constant $= -\ln a$

$$\ln\frac{a}{a-x} = y\frac{k}{k'}, \quad \text{or}$$

$$y = \frac{k'}{k}\,\ln\frac{a}{a-x}$$

Substituting this value of y, in (2)

$$\frac{dx}{dt} = k\,(a-x)\,\left(C - \frac{k'}{k}\ln\frac{a}{a-x}\right)$$

$$k = \frac{1}{C}\left(\frac{1}{(a-x)}\,\frac{dx}{dt} - k'\,\ln\frac{a-x}{a}\right) \quad . \; . \; . \; . \quad (5)$$

In this equation, excepting k, k' all other quantities can be directly obtained from the optical rotations of the mixture during the reaction, and from the known values of the amount of the ester and the concentration of the catalyst initially. If two such equations are obtained for different times, k' may be eliminated and the value of k found. The times selected for this calculation are placed in brackets in the last columns of the tables. In making the calculation the naperian logarithm may be used instead of the natural logarithm as the conversion factor is eliminated with k'. Moreover, since the value of k is unchanged by putting px for x and pa for a, a and x may be expressed in any units.

Reaction of type (3).—As the change in the strength of the catalyst is brought about by the formation of the methyl alcohol during the reaction, it is directly proportional to the amount of change x in the ester. Hence

$$\frac{dy}{dt} = k'\,x\,(C-y) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (6).$$

$$\frac{dx}{dt} = k\,(a-x)\,(C-y) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2).$$

On dividing (2) by (6),

$$\frac{dx}{dy}=\frac{k}{k'}\,\frac{a-x}{x}$$

$$\frac{x}{a-x}\,dx = \frac{k}{k'}\,dy$$

$$\frac{a-(a-x)}{a-x}\,dx = \frac{k}{k'}\,dy$$

$$-a \ln (a-x) - x = \frac{k}{k'}\,y + \text{a constant} \quad . \; . \; . \; . \quad (7).$$

When $x=0$, $y=0$, then the constant is, $-a \ln a$. Substituting the value of this constant in (7) and the value of y so obtained in (2), we get,

$$\frac{dx}{dt} = k\,(a-x)\,\left(C + \frac{k'}{k}\;x\;a \ln \frac{a-x}{a}\right)$$

$$k = \frac{1}{C}\,\left(\frac{1}{a-x}\,\frac{dx}{dt} - k'x - k'\,a \ln \frac{a-x}{a}\right) \quad . \; . \; . \; . \; . \quad (8).$$

k can be calculated according to this formula by taking two sets of values at different times and eliminating k'. The natural logarithm must be used in the calculation and if k' is assigned a definite value k will vary with the units in which x and a are expressed. If however pa is written for a and px for x the equation becomes

$$k = \frac{1}{C}\left\{\frac{1}{a-x}\,\frac{dx}{dt} - pk'\,\left(x + a \ln \frac{a-x}{a}\right)\right\}$$

so that on eliminating k' p also disappears indicating that the result is independent of the units used.

Abbreviations.

D = Date on which the observation of the optical rotations of the alcoholysis mixture was begun.

R = Ratio of the molecules of alcohol to ester in the mixture. The only significance of this ratio is to show that alcohol is always in large excess of the ester and that, consequently, the reaction is unimolecular.

C = Concentration of the hydrogen chloride in the alcoholysis mixture at start. Usually this concentration diminishes as the reaction proceeds, and where this is appreciable its value at the end of the observed period of the experiment is shown in brackets.

r = Rotation in degrees of the alcoholysis mixture contained in a two-decimetre tube.

a = Change in the amount of ester due to alcoholysis in a time counted from the moment the alcoholysis mixture was made, and expressed as grams per 20 cc.

t = Time in minutes. Mean time between any two consecutive readings or two readings not too far apart, and at which the rate of change has been derived and given in the next column.

ln = logarithm to the base e.

k = is the velocity constant of the reaction calculated for unit strength of catalyst.

All the reactions have been carried out at a temperature of 30°C.

REACTION I.

Menthyl Butyrate + Methyl Alcohol.

(1) D: 11 – 11 — 20 R = 44 C = 0·02434 N.

Time in minutes t	Rotation in Degrees r	Change in r	Change in t	T (mean time)	$\text{Log}\frac{\text{change in } r}{\text{change in } t}$
70	16·56	...	...	...	...
610	15·83	...	...	...	...
1280	15·02	1·54	1210	675	$\bar{3}{\cdot}105$
2050	14·16	1·67	1440	1330	$\bar{3}{\cdot}065$
2880	13·46	1·56	1600	2080	$\bar{4}{\cdot}990$
3570	12·84	1·32	1520	2810	$\bar{4}{\cdot}940$
4360	12·28	1·18	1480	3620	$\bar{4}{\cdot}900$
4920	11·88	0·96	1350	4245	$\bar{4}{\cdot}855$
5860	11·36	0·92	1500	5110	$\bar{4}{\cdot}790$
7260	10·79	1·09	2340	6090	$\bar{4}{\cdot}670$
8890	10·15	1·21	3030	7375	$\bar{4}{\cdot}600$

$k = 70{\cdot}7 \times 10^{-4}$

REACTION I.—(*continued.*)

Menthyl Butyrate + *Methyl Alcohol.*—(continued.)

(2) D : 18 – 2 – 2   R = 42   C = 0·2238 N. – (0·2220 N).

Time in minutes t	Rotation in Degrees r	Change in r	Change in t	T (mean time)	$\text{Log}\frac{\text{change in } r}{\text{change in } t}$
33	17·15	...	...	...	...
62	16·88	...	...	...	...
103	16·34	0·81	70	78	$\bar{2}$·063
158	15·78	1·10	96	110	$\bar{2}$·060
225	15·10	1·24	122	165	$\bar{2}$·007
281	14·53	1·25	123	219	$\bar{2}$·007
343	13·99	1·11	118	285	$\bar{3}$·973
410	13·49	1·04	129	345	$\bar{3}$·903
460	13·13	0·86	117	402	$\bar{3}$·863
545	12·57	0·92	135	478	$\bar{3}$·833
688	11·84	1·29	228	575	$\bar{3}$·755
1327	9·75	2·09	639	1008	$\bar{3}$·514
2013	8·84	0·91	686	1670	$\bar{3}$·122

$k = 62 \times 10^{-4}$

(3) D : 25 – 2 – 21   R = 46   C = 0·3844 N – (0·3753 N).

28	15·75	...	...	...	...
41	15·53	...	...	...	...
72	14·97	0·78	44	50	$\bar{2}$·250
115	14·22	1·31	74	78	$\bar{2}$·248
189	13·18	1·04	74	152	$\bar{2}$·148
300	11·91	1·27	111	245	$\bar{2}$·060
425	10·82	1·09	125	362	$\bar{3}$·940
568	9·93	0·89	143	496	$\bar{3}$·795
660	9·47	1·35	235	542	$\bar{3}$·760
1300	8·07	1·40	640	980	$\bar{3}$·340

$k = 62 \times 10^{-4}$

REACTION II.

Menthyl Crotonate + Methyl Alcohol.

(1) D: 2—3—21 R = 45 C = 0·4717 N. – (0·4135 N.)

Time in minutes t	Rotation in Degrees r	Change in r	Change in r × 0·2025 = x in grams per 20 cc.	$a-x$ in grams	$\frac{d(a-x)}{dt} \times 10^{-4}$	$\frac{10^4 d(a-x)}{a-x\,dt}$	$\log\frac{a}{a-x}$	$k.10^4$
...	18·22	...	...	2·165	...	...	...	...
500	16·87	1·35	0·273	1·892	4·96	2·62	0·059	5·86 (500,2000)
1000	15·77	2·45	0·496	1·669	4·07	2·44	0·113	5·64 (1000,2000)
1500	14·86	3·36	0·688	1·485	...	...	...	...
2000	14·06	4·16	0·842	1·323	2·96	2·24	0·213	5·38 (2000,4000)
2500	13·40	4·82	0·976	1·189	...	...	...	...
3000	12·82	5·40	1·092	1·072	2·19	2·04	0·304	5·67 (1000,3000)
3500	12·32	5·90	1·195	0·970	...	...	...	...
4000	11·87	6·35	1·285	0·880	1·75	1·99	0·390	5·56 (1000,4000)
4500	11·47	6·75	1·370	0·795	...	...	...	...

$k = 5·62 \times 10^{-4}$

(2) D: 3—3—21 R = 42 C = 0·5405 N. – (0·4877 N.)

...	16·95	...	...	2·012	...	...	...	...
250	16·10	0·85	0·172	1·840	...	...	...	...
500	15·41	1·54	0·312	1·700	5·26	3·095	0·073	5·96 (500,4500)
750	14·80	2·15	0·435	1·577	4·62	2·930	0·106	...
1000	14·27	2·68	0·542	1·470	4·13	2·810	0·133	...
1250	13·78	3·17	0·642	1·370	3·80	2·780	0·167	5·57 (1250,3000)
1500	13·33	...	...	...	...	...	...	...
2000	12·56	4·39	0·890	1·122	2·89	2·570	0·253	5·35 (2000,4000)
2500	11·90	5·05	1·025	0·987	2·49	2·525	0·310	...
3000	11·33	5·62	1·140	0·872	2·11	2·420	0·362	...
3500	10·86	6·09	1·235	0·777	1·80	2·320	0·413	5·53 (1000,3500)
4000	10·44	6·51	1·320	0·692	1·60	2·310	0·463	...
4500	10·07	6·88	1·395	0·617	1·40	2·270	0·513	5·48 (1000,4500)

$k = 5·6 \times 10^{-4}$

REACTION III.

Menthyl Hydrocinnamate + *Methyl Alcohol.*

(1) D: 14—4—21 R = 40 C = 0·5784 N.—(0·5644 N.)

Time in minutes t	Rotation in Degrees r	Change in r	Change in t	T	$\text{Log}\frac{\text{change in } r}{\text{change in } t}$
31	13·85	...	...	...	...
96	12·58	1·27	65	63	$\bar{2}$·300
172	11·37	1·21	76	134	$\bar{2}$·202
245	10·39	0·98	73	208	$\bar{2}$·128
362	9·22	1·17	117	303	$\bar{2}$·000
459	8·49	0·73	97	410	$\bar{3}$·876
522	8·15	...	...	...	...
668	7·51	0·98	209	563	$\bar{3}$·670
758	7·27	0·88	236	640	$\bar{3}$·572

$k = 51{\cdot}7 \times 10^{-4}$

(2) D: 14—4—21 R = 70 C = 0·4598 N.—(0·4546 N.)

46	8·87	...	...	...	...
85	8·44	0·43	39	65	$\bar{2}$·043
186	7·44	1·00	101	135	$\bar{3}$·995
258	6·87	0·57	172	222	$\bar{3}$·898
370	6·17	0·70	112	314	$\bar{3}$·795
452	5·76	...	...	...	...
528	5·44	0·73	158	449	$\bar{3}$·665
661	5·06	0·70	209	556	$\bar{3}$·525

$k = 52{\cdot}0 \times 10^{-4}$

REACTION IV.

Menthyl Cinnamate and Methyl Alcohol.

(1) D : 8—4—21 R = 44 C = 0·5480 N. – (0·4852 N).

Time in minutes t	Rotation in Degrees r	Change in r	Change in $r \times 0{\cdot}203 = x$ in grams per 20 cc.	$a - x$ in grams	$\frac{d(a-x)}{dt} \times 10^4$	$\frac{10^4}{a-x} \cdot \frac{d(a-x)}{dt}$	$\log \frac{a}{a-x}$	$k.\ 10^4$
0	19·10	...	...	2·490	...	...	...	...
250	18·37	...	...	...	...	...	...	...
500	17·77	1·33	0·270	2·220	4·58	2·070	0·049	3·95 (500, 2000)
750	17·24	...	...	...	...	...	...	...
1000	16·74	2·36	0·478	2·012	3·94	1·955	0·092	3·74 (1000, 3000)
1500	15·83	3·27	0·663	1·827	3·51	1·920	0·134	...
2000	15·01	4·09	0·830	1·660	3·11	1·825	0·175	...
2500	14·30	4·80	0·973	1·517	2·76	1·820	0·215	3·77 (1000, 2500)
3000	13·65	5·45	1·106	1·384	2·48	1·790	0·255	...
3500	13·08	6·02	1·222	1·268	2·17	1·715	0·293	3·92 (1000, 3500)
4000	12·58	6·52	1·322	1·168	...	...	...	...

$k = 3{\cdot}85 \times 10^{-4}$

(2) D : 9—4—21 R = 47 C = 0·4088 N.—(0·3714 N).

0	18·00	...	...	2·350	...	...	...	...
250	17·51	...	...	...	...	...	...	...
500	17·06	0·94	0·191	2·159	3·58	1·660	0·037	4·18 (500, 3500)
750	16·63	...	...	...	...	...	...	...
1000	16·24	1·76	0·357	1·993	3·14	1·575	0·085	...
1500	15·51	2·49	0·505	1·845	2·80	1·515	0·105	...
2000	14·86	3·14	0·637	1·713	2·52	1·470	0·137	3·85 (2000, 3500)
2500	14·27	3·73	0·757	1·593	2·30	1·440	0·169	...
3000	13·73	4·27	0·867	1·483	2·09	1·410	0·200	...
3500	13·24	4·76	0·966	1·384	1·94	1·400	0·229	4·12 (1000, 3500)
4000	12·77	5·23	1·061	1·289	...	...	...	...

$k = 4{\cdot}05 \times 10^{-4}$

REACTION IV—(*continued.*)

Menthyl Cinnamate and Methyl Alcohol.—(continued.)

(3). D : 18—4—21 R = 52 C = 0·5832 N.—(0·5280 N).

(*N.B.*—To the alcohol has been added 10 per cent of benzene by volume to see if benzene has any effect on the rate of alcoholysis).

Time in minutes t	Rotation in Degrees r	Change in r	Change in r × 0·203 $=x$ in grams per 20 cc.	$a - x$ in grams	$\frac{d(a-x)}{dt} \times 10^4$	$\frac{10^4}{a-x} \times \frac{d(a-x)}{dt}$	$\log \frac{a}{a-x}$	$k . 10^4$
0	15·20	...	...	1·980	...	...	...	...
250	14·65	0·55	0·112	...	...	...	...	...
500	14·16	1·04	0·211	1·769	3·82	2·160	0·049	3·88 (500, 3500)
750	13·71	1·49	0·303	...	...	...	...	...
1000	13·28	1·92	0·390	1·590	3·31	2·082	0·095	...
1500	12·53	2·67	0·542	1·438	2·60	1·950	0·138	...
2000	11·90	3·30	0·670	1·310	2·35	1·800	0·179	3·94 (2000, 500)
2500	11·37	3·83	0·777	1·203	2·10	1·715	0·216	...
3000	10·87	4·33	0·880	1·100	1·93	1·755	0·255	...
3500	10·42	4·78	0·970	1·010	1·65	1·670	0·292	3·98 (3500, 1500)
4000	10·04	5·16	1·045	0·935	...	...	...	...

$k = 3·93 \times 10^{-4}$

(4) D : (18—4—21) R = 52 C = 0·5832 N.—(0·5280 N).

N.B.—Here no benzene has been added.

0	16·25	0	0	2·115	...	...	...	...
250	15·63	0·62	0·126	1·989	...	...	...	...
500	15·08	1·17	0·237	1·878	4·34	2·31	0·052	4·13 (500, 3500)
750	14·56	1·69	0·343	1·772	...	...	...	...
1000	14·09	2·16	0·438	1·677	3·73	2·22	0·101	...
1500	13·25	3·00	0·610	1·505	3·10	2·05	0·148	3·9 (1500, 3500)
2000	12·57	3·68	0·748	1·367	2·60	1·90	0·189	...
2500	11·97	4·28	0·870	1·245	2·34	1·875	0·230	...
3000	11·42	4·83	0·982	1·133	2·12	1·860	0·271	...
3500	10·93	5·32	1·082	1·033	1·83	1·81	0·311	4·1 (3500, 1000)
4000	10·50	5·75	1·165	0·950	...	...	...	...

REACTION V.

Methyl Butyrate + Menthol (with 10 per cent benzene by volume)

(1) D: 23—6—21 R = 9·8 C = 0·6930 N.—(0·6625 N.)

$t/60$	Rotation in Degrees r	Change in r	Change in $r \times 0{\cdot}129 = x$ in grams	$a - x$ in grams	$6{\cdot}10^3 \times \frac{d(a-x)}{dt}$	$\frac{6{\cdot}10^3}{a-x} \times \frac{d(a-x)}{dt}$	$a \ln \frac{a}{a-x}$	$k.\ 10^5$
0	75·00	...	...	1·0	...	...	...	...
25	75·71	0·71	0·092	0·908	...	...	...	...
50	76·36	1·36	0·176	0·825	0·315	0·382	0·195	...
75	76·93	1·93	0·249	0·751	...	...	...	...
100	77·45	2·45	0·316	0·684	0·258	0·377	0·379	10·0 (100,275)
125	77·93	2·93	0·378	0·622	...	...	...	...
150	78·55	3·55	0·458	0·572[1]	0·202	0·353	0·560	9·3 (150,50)
175	78·71	3·71	0·479	0·521	...	...	...	...
200	79·00	4·00	0·516	0·484	0·136	0·281	0·724	10·0 (200,100)
225	79·24	4·24	0·547	0·453	...	...	...	...
250	79·44	4·44	0·573	0·427	0·102	0·239	0·850	9·46 (250,50)
275	79·64	4·64	0·598	0·402	0·094	0·234	0·911	10·0 (275,200)
300	79·81	4·81	0·620	0·380	...	...	...	...

[1] Smoothed value.

$k = 9{\cdot}75 \times 10^{-5}$

(2) D: 12—7—21 R = 10 C = 1·010 N.—(0·9583 N.)

0	77·00	0	0	0·807	...	...	...	...
25	77·81	0·81	0·105	0·703	...	...	...	...
50	78·50	1·51	0·195	0·612	0·336	0·549	0·223	9·3 (50,300)
75	79·10	2·11	0·272	0·535	...	...	...	...
100	79·60	2·62	0·338	0·469	0·238	0·507	0·439	...
125	80·01	3·03	0 391	0·416	...	...	...	...
150	80·35	3·38	0·436	0·371	0·160	0·432	0·628	9·36 (150,50)
175	80·61	3·65	0·471	0·336	...	...	...	...
200	80·84	3·89	0·502	0·305	0·112	0·368	0·785	...
225	81 03	4 08	0·527	0·280	...	...	...	...
250	81·21	4·27	0·552	0·255	0·092	0·361	0·925	9·23 (250,100)
275	81·37	4·44	0·573	0·234	...	...	...	
300	81·50	4·58	0·591	0·216	0·066	0·306	01·06	8·63 (300,150)
325	81·61	4·69	0·606	0·201	...	...	...	...
350	81·69	4·78	0·617	0·190	...	...	...	...

$k = 9{\cdot}13 \times 10^{-5}$

REACTION VI.

Methyl Crotonate + Menthol (with 10 per cent benzene by volume.)

D : 12—7—21 R = 13 C = 1·010 N.—(0·832 N.)

$t/60$	Rotation in Degrees r	Change in r	Change in $r \times 0{\cdot}0904 = x$ in grams	$a-x$ in grams	$6\times10^3 \times \frac{d(a-x)}{dt}$	$\frac{6\cdot10^5}{a-x} \times \frac{d(a-x)}{dt}$	$\ln \frac{a}{a-x}$	$k\cdot10^6$
0	76·88	0	0	0·858	...	...	...	...
100	77·39	0·51	0·046	0·812	0·044	5·42	0·048	9·82 (1000, 100)
200	77·85	0·97	0·088	0·770	0·040	5·13	0·093	9·65 (200, 800)
300	78·26	1·38	0·125	0·733	...	...	...	...
400	78·62	1·74	0·157	0·701	0·031	4·35	0·174	...
500	78·94	2·06	0·186	0·672	...	...	...	...
600	79·22	2·34	0·211	0·647	0·024	3·71	0·245	9·82 (600, 200)
700	79·47	2·59	0·234	0·624	...	...	...	...
800	79·71	2·83	0·256	0·602	0·019	3·16	0·306	...
900	79·89	3·01	0·272	0·586	...	...	...	...
1000	80·07	3·19	0·288	0·570	0·015	2.635	0·350	9·58 (200, 1000)
1100	80·23	3·35	0·303	0·555	...	...	...	...
1200	80·40	3·52	0·318	0·540	...	...	...	...

$k = 9{\cdot}72 \times 10^{-6}$

REACTION VII.

Ethyl Butyrate + Menthol (with ten per cent. benzene by volume)

D = 21—8—21 R = 14·8 C = 1·050 N — (1·010 N)

$t/60$	Rotation in Degrees r	Change in r	Change in $t/60$	T	$\log\frac{\text{change in } r}{\text{change in } t}$
2·0	76·85	...	...	...	...
19·0	77·16	...	...	...	...
48·0	77·70	0·85	46·0	25	$\bar{2}$·267
71·5	78·00	0·84	52·5	45	$\bar{2}$·205
90·0	78·30	...	...	...	...
116·2	78·58	0·88	68·2	82	$\bar{2}$·110
139·2	78·95	0·95	67·7	105·5	$\bar{2}$·147
163·2	79·16	0·86	73·2	127·0	$\bar{2}$.070
187·2	79·44	0·86	71·0	152·0	$\bar{2}$·083
212·2	79·63	0·68	73·0	176·0	$\bar{3}$·970
236·2	79·83	0·67	73·0	200·0	$\bar{3}$·963
287·0	80·22	0·78	99·8	237·0	$\bar{3}$.893
309·2	80·43	0·80	97·0	261·0	$\bar{3}$·915
380·7	80·65	0·82	144·5	308·5	$\bar{3}$·755
409·5	80·87	0·65	122·5	348·2	$\bar{3}$·725
451·2	81·09	0·66	142·0	380·2	$\bar{3}$·667
499·2	81·23	0·36	89·7	454·5	$\bar{3}$·603

$k = 0·585 \times 10^{-4}$

TABLE

REACTION	Number and Date of Experiment = D	$\frac{\text{Number of Alcohol Mols}}{\text{Number of Ester Mols}} = R$
I. Menthyl Butyrate + Methyl Alcohol.	(1) 11-11-1920	44
	(2) 18- 2-1921	42
	(3) 25- 2-1921	46
III. Menthyl Hydrocinnamate + Methyl Alcohol.	14- 4-1921	40
	14- 4-1921	70
VII. Ethyl Butyrate + Menthol.	21- 8-1921	14·8
II. Menthyl Crotonate + Methyl Alcohol.	(1) 2- 3-1921	45
	(2) 3- 3-1921	42
IV. Menthyl Cinnamate + Methyl Alcohol.	(1) 8- 4-1921	44
	(2) 9- 4-1921	47
	(3) 18- 4-1921	52
	(4) 18- 4-1921	52
V. Methyl Butyrate + Menthol	(1) 23- 6-1921	9·8
	(2) 12- 7-1921	10·9
VI. Methyl Crotonate + Menthol.	12-7-1921	13·0

V.

Normality of hydrogen chloride = C	Velocity constant for normal Catalyst at 30·C $k.10^6$	Formula used to calculate k
0·02434	7070	$k = \frac{1}{C} \frac{1}{T_{3\cdot2} - T_{2\cdot1}} \log \frac{X_{2\cdot1}}{X_{3\cdot2}} \quad \ldots (1)$
0·2238	6200	
0·3844	6200	
0·5784	5170	
0·4598–	5200	
1·054–(1·010)	58	
0·4717–(0·4135)	562	$k = \frac{1}{C} \left\{ \frac{1}{a-x} \frac{dx}{dt} - k' \ln \frac{a-x}{a} \right\} \quad \ldots (5)$
0·5405–(0·4877)	560	
0·5480–(0·4852)	385	
0·4088–(0·3714)	405	
0·5832–(0·5280)	393	
0·5832–(0·5280)	404	
0·6930–(0·6625)	97·5	$k = \frac{1}{C} \left\{ \frac{1}{a-x} \frac{dx}{dt} - k'x - k'a \ln \frac{a-x}{a} \right\} \quad \ldots (8)$
1·010 –(0·9583)	91·3	
1·010 –(0·832)	9·72	

Table VI gives the velocity constants of alcoholysis for the reactions along with the results reported in a previous paper.[1]

TABLE VI.

Alcoholysis Constants.

Composition of initial mixture				Alcoholysis Constant for normal hydrogen chloride at 30° C $k \cdot 10^6$
Menthyl	Butyrate	+	Methyl Alcohol	6200
,,	Crotonate	+	,, ,, ...	561
,,	Hydrocinnamate	+	,, ,, ...	5185
,,	Cinnamate	+	,, ,, ...	397
Ethyl	Butyrate	+	,, ,, ...	90200
,,	Crotonate	+	,, ,, ...	6250
,,	Hydrocinnamate	+	,, ,, ...	78000
,,	Cinnamate	+	,, ,, ...	3900
,,	Butyrate	+	Menthol	58
Methyl	Butyrate	+	,, ...	94·4
,,	Crotonate	+	,, ...	9·7
,,	Butyrate	+	Ethyl Alcohol	19800
,,	Crotonate	+	,, ,, ...	1400
,,	Hydrocinnamate	+	,, ,, ...	19100
,,	Cinnamate	+	,, ,, ...	1075

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[1] B. Dasannacharya and J. J. Sudborough, *loc. cit.*

IV. DISCUSSION OF RESULTS

1. An $\alpha\beta$-olefinic linkage in the acyl group of an ester exerts a strong retarding influence in the alcoholysis of the ester, as shown in Table VII.

TABLE VII.

Velocity constant	Alcoholysis	Esterification	Hydrolysis
(a) $\frac{k\text{ (menthyl butyrate, methyl alcohol)}}{k\text{ (menthyl crotonate, methyl alcohol)}} =$	11·05	...	...
(b) $\frac{k\text{ (menthyl hydrocinnamate, methyl alcohol)}}{k\text{ (menthyl cinnamate, methyl alcohol)}} =$	13·05	...	...
(c) $\frac{k\text{ (methyl butyrate, menthol)}}{k\text{ (methyl crotonate, menthol)}} =$	9·73	...	...
(d) $\frac{k\text{ (ethyl butyrate, methyl alcohol)}}{k\text{ (ethyl crotonate, methyl alcohol)}} =$	14·5	...	29[3]
(e) $\frac{k\text{ (ethyl hydrocinnamate, methyl alcohol)}}{k\text{ (ethyl cinnamate, methyl alcohol)}} =$	20·0	36·0[1]	30[3]
(f) $\frac{k\text{ (methyl butyrate, ethyl alcohol)}}{k\text{ (methyl crotonate, ethyl alcohol)}} =$	13·6	39·0[2]	...
(g) $\frac{k\text{ (methyl hydrocinnamate, ethyl alcohol)}}{k\text{ (methyl cinnamate, ethyl alcohol)}} =$	17·8	50·5[2]	...
Mean ...	14·2	41·8	29·5

The retardation, as can be seen is of the same order, under alcoholysis, the mean value being 14·2. For comparison values for the retardation in esterification and hydrolysis are also given, in cases where the velocity constant is known, the mean values being 41·8 and 29·5 respectively.

The retardation in alcoholysis is somewhat less with menthyl esters or when menthol has been used than when methyl or ethyl esters and alcohols alone are involved.

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[1] Calculated from the values found by Anton Kailan, *Monatsh*, 1907, **28**, 1143, 1153.

[2] Calculated from the values determined by Sudborough and Roberts, *J. Chem. Soc.*, 1909, **95**, 315.

[3] Sudborough and Williams, *ibid.*, 1912, **101**, 412.

2. The replacement of a β-methyl by a phenyl group increases the retardation, as shown by the ratios given in Table VIII.[1]

TABLE VIII.

$$(i)\ \frac{k\ \text{menthyl butyrate, methyl alcohol}}{k\ \text{menthyl hydrocinnamate, methyl alcohol}} = 1{\cdot}19$$

$$(j)\ \frac{k\ \text{menthyl crotonate, methyl alcohol}}{k\ \text{menthyl cinnamate, methyl alcohol}} = 1{\cdot}68$$

$$(k)\ \frac{k\ \text{ethyl butyrate, methyl alcohol}}{k\ \text{ethyl hydrocinnamate, methyl alcohol}} = 1{\cdot}16$$

$$(l)\ \frac{k\ \text{ethyl crotonate, methyl alcohol}}{k\ \text{ethyl cinnamate, methyl alcohol}} = 1{\cdot}60$$

$$(m)\ \frac{k\ \text{methyl butyrate, ethyl alcohol}}{k\ \text{methyl hydrocinnamate, ethyl alcohol}} = 1{\cdot}04$$

$$(n)\ \frac{k\ \text{methyl crotonate, ethyl alcohol}}{k\ \text{methyl cinnamate, ethyl alcohol}} = 1{\cdot}30$$

3. A comparison of the values given in Table VIII shows that the ratio $(j) > (i)$, $(l) > (k)$ and $(n) > (m)$ indicating that the influence of the group attached to the β-carbon atom is more pronounced when there is an olefinic linkage in the αβ-position.

4. The influence of the alkyls in the substituted carboxyl, when the alcohol remains the same, is as follows :—

$$(o)\ \frac{k\ \text{ethyl butyrate, methyl alcohol}}{k\ \text{menthyl butyrate, methyl alcohol}} = 14{\cdot}6$$

$$(p)\ \frac{k\ \text{ethyl crotonate, methyl alcohol}}{k\ \text{menthyl crotonate, methyl alcohol}} = 11{\cdot}2$$

$$(q)\ \frac{k\ \text{ethyl hydrocinnamate, methyl alcohol}}{k\ \text{menthyl hydrocinnamate, methyl alcohol}} = 15{\cdot}0$$

$$(r)\ \frac{k\ \text{ethyl cinnamate, methyl alcohol}}{k\ \text{menthyl cinnamate, methyl alcohol}} = 9{\cdot}9$$

$$(s)\ \frac{k\ \text{methyl butyrate, menthol}}{k\ \text{ethyl butyrate, menthol}} = 1{\cdot}63$$

5. The ratio of the constants for the direct and the reverse reaction is practically independent of the nature of the acids, as was shown by Kolhatkar.[2]

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[1] The same generalization is arrived at by a comparison of the ratios given in Table VII, e.g $\frac{(b)}{(a)} = 1{\cdot}18$, $\frac{(e)}{(d)} = 1{\cdot}38$ and $\frac{(g)}{(f)} = 1{\cdot}31$.

[2] *Ibid.*

For the interchanging of menthyl and methyl groups the values are, as follows :—

$$(t)\quad \frac{k\text{ menthyl butyrate, methyl alcohol}}{k\text{ methyl butyrate, menthol}} = 65{\cdot}7$$

$$(u)\quad \frac{k\text{ menthyl crotonate, methyl alcohol}}{k\text{ methyl crotonate, menthol}} = 58{\cdot}0$$

Mean value = 62

And for the interchange of methyl and ethyl groups, as follows :—

$$(v)\quad \frac{k\text{ ethyl butyrate, methyl alcohol}}{k\text{ methyl butyrate, ethyl alcohol}} = 4{\cdot}6$$

$$(w)\quad \frac{k\text{ ethyl crotonate, methyl alcohol}}{k\text{ methyl crotonate, ethyl alcohol}} = 4{\cdot}4$$

$$(x)\quad \frac{k\text{ ethyl hydrocinnamate, methyl aloohol}}{k\text{ methyl hydrocinnamate, ethyl alcohol}} = 4{\cdot}1$$

$$(y)\quad \frac{k\text{ ethyl cinnamate, methyl alcohol}}{k\text{ methyl cinnamate, ethyl alcohol}} = 3{\cdot}6$$

Mean value = 4·2

In conclusion I wish to thank Dr. Sudborough for suggesting the research and both Dr. Sudborough and Dr. H. E. Watson for valuable suggestions in connection with it. This work was carried out in the laboratories of the Indian Institute of Science, at Bangalore and my obligations are also due to the Institute for the grant of a scholarship which enabled me to conduct it there. My thanks are also due to Professor K. F. Herzfild of the University of Munich, for valuable suggestions.

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APPENDIX.

NOTES ON CALCULATIONS.

By H. E. Watson.

The equation (3) p. 8 may be solved and k' evaluated by means of the figures given in Table III, p. 6.

If this is done we obtain

$(C-y)/C = e^{-k't}$ k' being approximately $1{\cdot}7 \times 10^{-5}$

substituting in equation (2)

$$\frac{dx}{dt} = Ck(a-x)e^{-k't}$$

the solution of which is

$$k' \ln a/(a-x) = kC\left(1 - e^{-k't}\right) \ldots\ldots (5')$$

from which k may be calculated.

Table A shows some comparative values for reaction II (1) (a_1) calculated according to equation (5), with $k' = 1{\cdot}7 \times 10^{-5}$, ($a_2$) the same with $k' = 10 \times 10^{-5}$; (*b*) calculated in the ordinary way for a unimolecular reaction neglecting the change in concentration of the catalyst and (*c*) the figures shown under the heading ‘ reaction II ’.

TABLE A.

Comparative values of $k.10^4$.

Time	(a_1)	(a_2)	(*b*)	(*c*)
500	5·70	5·85	5·70	5·86
1000	5·51	5·80	5·51	5·64
2000	5·29	5·76	5·22	5·38
3000	5·07	5·75	4·96	5·67
4000	4·91	5·78	4·76	5·56

From the values given under (*b*) it will be seen that there is a considerable fall in the value of k if the reaction is regarded as a simple unimolecular one. On the other hand, these values are not greatly altered by applying a correction for the observed change in the concentration of catalyst (a_1), and there is still a very marked drop in the value of k. A remarkably good constant is obtained if k' is given the empyrical value 10×10^{-5}. This indicates that the fall in the effective concentration of the catalyst is some six times the observed rate. This value is certainly well outside the limit of experimental error in determining the concentration of hydrochloric acid, and it appears that there must be an additional cause of retardation of the reaction.

It has been shown by Kolhatkar[1] that small quantities of water greatly diminish the reaction velocity, 0·14 per cent. reducing the velocity constant in the case of ethyl acetate and methyl alcohol by 25 per cent. In the present series of reactions the conversion of methyl alcohol into methyl chloride is accompanied by liberation of water, a decrease of 0·1 in the normality corresponding with the production of 0·18 per cent. of water. The observed changes in concentration of hydrochloric acid varied from about 0·03N to 0·18N so that it is evident that this production of water will have a considerable influence on the reaction velocity. The empyrical value selected for k' thus probably is the constant for a reaction representing the combined effect of the diminution in concentration of the acid and the retarding influence of the water produced, upon the main reaction.

In the case of the reactions of type III for which equation (8) which may be written

$$kC = \frac{1}{a-x}\frac{dx}{dt} + k'\left(a \ln \frac{a}{a-x} - x\right)$$

has been deduced, the value of k depends upon the units in which a and x are expressed, but as already pointed out (p. 10) it is only the second term which is affected and by varying k' according to the units used the value of k will be unchanged.

If k' is put equal to $8{\cdot}5 \times 10^{-5}$ and k calculated by the above equation from the figures given under reaction V a very satisfactory constant is obtained as shown under (b) Table B. An equally good value is obtained if k' is put equal to 3×10^{-5} and equation 5' use
as shown under (c) so that the experiments are not sufficiently accur
~~to~~ show which, if either, equation is strictly correct. Columns
The ~~object of~~ ıble B show the values of k when $k' = 0$, i.e. when
to discover whetbumed to be of the ordinary unimolecular type, anc
comparausly given.

TABLE B.

Values of k calculated by different methods. Reaction V.

Time	(*a*) $k' = 0$	(*b*) Equation 8	(*c*) Equation 5′	(*d*) Elimination
50	9·3	9·4	9·7	...
100	9·1	9·8	10·0	10·0
150	9·0	9·7	10·2	9·3
200	8·7	9·3	10·4	10·0
250	8·3	9·2	10·3	9·5
275	8·0	9·4	10·1	10·0

In reaction VI, $k' = 7{\cdot}5 \times 10^{-5}$ gives the best values for k when calculated by means of equation 8.

Since it would be difficult to interpret the physical meaning of equation (5′) when appplied to reactions of type III it appears probable that (8) is the correct equation with the limitation that k' is not merely the velocity constant for the diminution in concentration of the catalyst, but a constant which allows for this diminution and also for the effect of the water formed in the reaction.