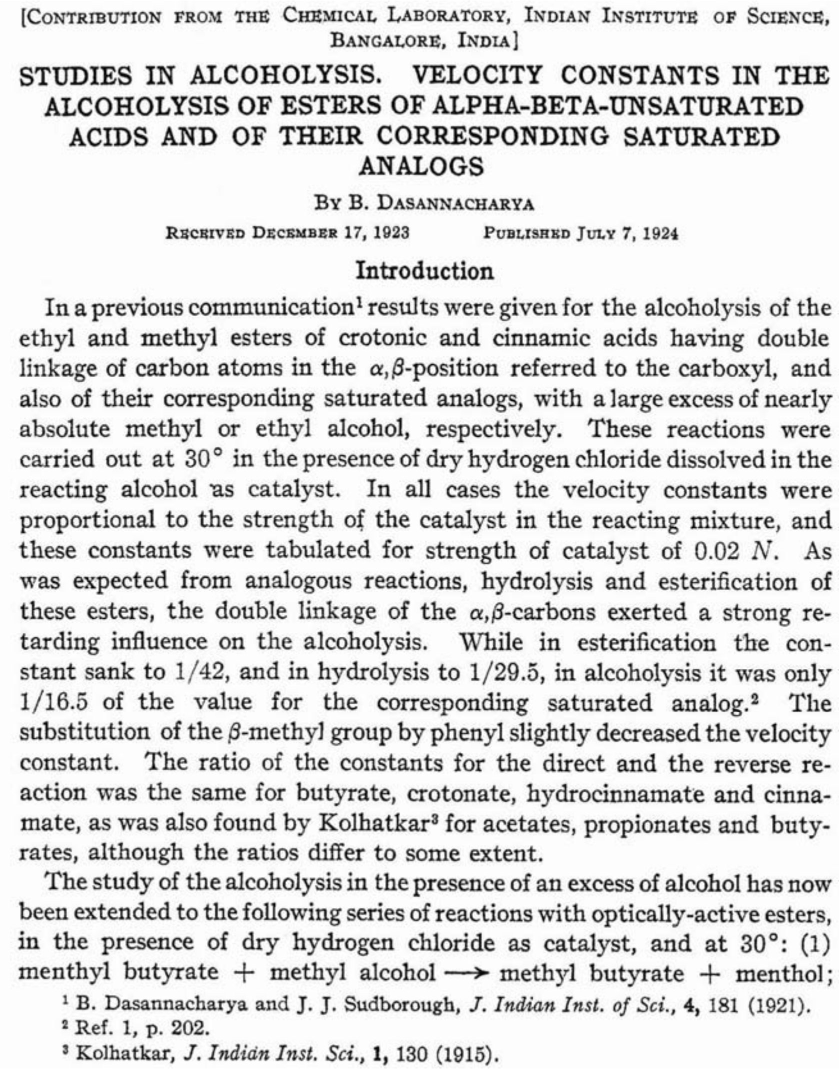

[CONTRIBUTION FROM THE CHEMICAL LABORATORY, INDIAN INSTITUTE OF SCIENCE, BANGALORE, INDIA]

STUDIES IN ALCOHOLYSIS. VELOCITY CONSTANTS IN THE ALCOHOLYSIS OF ESTERS OF ALPHA-BETA-UNSATURATED ACIDS AND OF THEIR CORRESPONDING SATURATED ANALOGS

BY B. DASANNACHARYA

RECEIVED DECEMBER 17, 1923   PUBLISHED JULY 7, 1924

Introduction

In a previous communication[1] results were given for the alcoholysis of the ethyl and methyl esters of crotonic and cinnamic acids having double linkage of carbon atoms in the α,β-position referred to the carboxyl, and also of their corresponding saturated analogs, with a large excess of nearly absolute methyl or ethyl alcohol, respectively. These reactions were carried out at 30° in the presence of dry hydrogen chloride dissolved in the reacting alcohol 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 strength of catalyst of 0.02 N. As was expected from analogous reactions, hydrolysis and esterification of these esters, the double linkage of the α,β-carbons exerted a strong retarding influence on the alcoholysis. While in esterification the constant sank to 1/42, and in hydrolysis to 1/29.5, in alcoholysis it was only 1/16.5 of the value for the corresponding saturated analog.[2] The substitution of the β-methyl group by phenyl slightly decreased the velocity constant. The ratio of the constants for the direct and the reverse reaction was 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.

The study of the alcoholysis in the presence of an excess of alcohol has now been extended to the following series of reactions with optically-active esters, in the presence of dry hydrogen chloride as catalyst, and at 30°: (1) menthyl butyrate + methyl alcohol ⟶ methyl butyrate + menthol;

[1] B. Dasannacharya and J. J. Sudborough, *J. Indian Inst. of Sci.*, **4**, 181 (1921).

[2] Ref. 1, p. 202.

[3] Kolhatkar, *J. Indian Inst. Sci.*, **1**, 130 (1915).

(2) menthyl crotonate + methyl alcohol ⟶ methyl crotonate + menthol; (3) menthyl hydrocinnamate + methyl alcohol ⟶ methyl hydrocinnamate + menthol; (4) menthyl cinnamate + methyl alcohol ⟶ methyl cinnamate + menthol; (5) methyl butyrate + menthol ⟶ menthyl butyrate + methyl alcohol; (6) methyl crotonate + menthol ⟶ menthyl crotonate + methyl alcohol; (7) ethyl butyrate + menthol ⟶ menthyl butyrate + ethyl alcohol.

The velocity constant in every case was calculated from the observed change in optical rotation of the reacting mixtures, corrections being applied for diminution of the velocity constant owing to a decrease 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 on the basis of normal strength of catalyst.

The work of Bruni and Contardi[4] may be here referred to; they studied polarimetrically the reactions of alkyl esters with menthol, but in the absence of a catalyst.

Jessie Elizabeth Minor[5] also used the polarimetric method to study the equilibrium concentrations when menthyl aceto-acetate was treated with a series of aliphatic alcohols and found that they vary only within fairly narrow limits at the high temperatures at which the reactions were studied, showing that the relative affinities of the various alcohol-alkyls for the hydroxyl and acid radicals are about the same. It was also pointed out that in the alcoholysis reaction where the alkyl radicals in the ester and alcohol are of similar constitution the equilibrium should not be far from 50%, provided equimolecular quantities react. The paper contains a critical survey of previous work and a list of the literature on alcoholysis, with the more important matter in an analytical form that is extremely useful for ready reference and comparison.

Experimental Part

The menthyl esters of butyric and crotonic acids have been prepared by the action of alkyl iodides with the silver salts of the acids. The general method employed for the preparation of the menthyl esters is the same as was used by Rupe[6] and his collaborators, with the difference that the intermediary products, namely, the chlorides of the acids, have been prepared by the action of thionyl chloride, $SOCl_2$, a reaction that takes place in the cold and is completed on warming. Sulfur dioxide is given off and the acid chloride is distilled.

Table I gives the more important constants of the products.

Methyl Alcohol

This was the same as was used in a previous investigation.[7] It was prepared by repeatedly dehydrating Kahlbaum's pure, acetone-free and

---

[4] Bruni and Contardi, *Atti accad. Lincei*, [5] **15,** 637 (1906); *Gazz. chim. ital.*, **36,** 356 (1906).

[5] Minor, *Dissertation*, Bryn Mawr College, **1917.**

[6] Rupe, *Ann.*, **369,** 319 (1909).

[7] Ref. 1, pp. 183, 201.

TABLE I

PREPARATION OF ESTERS

Substance	Boiling point		Specific rotation			
	Corr. °C.	Pressure in mm.	Rotation in degrees	Temp. °C.		Ref.
Menthyl butyrate	115–115.8	8.3	−69.53	28	no solvent	1
	126.6	12.5	−72.91	20	in alcohol	6
			−69.52	(′)	no solvent	8
Menthyl crotonate	124–125	9.5	−84.53	25	no solvent	1'
			−84.03	35		
			−83.51	45		
	134	11	−90.67	20	in benzene	6
	140–145.5	14	−91.06	20		
			−82.61	(′)	no solvent	8
Menthyl hydrocinnamate	181–182	5	−56.5	30	in benzene	1
	197–198	12	−58.48	20	in benzene	6
			−56.21	(′)	no solvent	8
Menthyl cinnamate	undistilled		−76.8	30	in benzene	1
			−75.32	20	in benzene	6
			−76.92	20		
			−86.65	(′)	no solvent	8
Menthol	42[a] m. p.		−47.2	25	in benzene	
Methyl butyrate	102.4–103.3	760	...	....		1
	102.8	760	...	....		9
Ethyl butyrate	119–120	760	...	....		1
	119.9	760	...	....		9
Methyl crotonate	118.6–119.6	760	...	....		1
	120.7	760	...	....		10

[a] Distilled at 10 mm. in a stream of dry air.

nearly absolute methyl alcohol with small amounts of metallic calcium until the distilled product did not alter in density on further treatment with calcium; d_4^{25}, 0.78658 (reduced to a vacuum); d_4^{25}, 0.78658 (Klasson and Norlin[11]).

In the previous investigation a higher value was given, as the alcoholysis of ethyl butyrate with the methyl alcohol indicated 0.05% of water, which might have been introduced with the catalyst (hydrogen chloride). It is feared that the same uncertainty exists regarding the present results also. It is well, however, to state that this quantity could not be large, as great care was taken to exclude water vapor. The gas was produced by the action of moderately concentrated sulfuric acid on anhydrous sodium chloride. The gas was led through two wash bottles containing pure, concd. sulfuric acid, before it was admitted to the alcohol. Atmospheric water vapor was excluded by using a calcium chloride tube. The alcohol and the alcoholic solution of the catalyst were always kept in a desiccator.

---

[8] Tschugaeff, *Chem. Centr.*, **73,** II, 1238 (1902).

[9] Schumann, *Ann. Phys. Chem.*, **12,** 48 (1882).

[10] Kahlbaum, *Ber.*, **12,** 344 (1879).

[11] Klasson and Norlin, *Arkiv. Kemi, Mineral. Geol.*, **2,** No. 24, 1 (1906).

Preparation of Mixtures for Alcoholysis

Hydrogen chloride prepared by the action of pure, concd. sulfuric acid was bubbled through bottles containing pure, concd. sulfuric acid and then into a flask containing the alcohol; a little cotton wool served to prevent acid spray from entering the alcohol flask. Contamination of the alcohol through atmospheric moisture was avoided by a calcium chloride tube. Equal volumes of the alcohol and the requisite ester were mixed and transferred to a 2-dm. polarimeter tube, which was fixed horizontally below the surface of the water in a toluene-regulated thermostat, at 30°. Both the ends of the tube protruded from the thermostat, but this could not have introduced any serious error, as the temperature of the surrounding air was not far from the temperature 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 interference.

Changes in Optical Rotation

The alcoholysis was followed by observing the change of optical rotation of the mixture for the yellow sodium light. This change should be exactly proportional to the extent of alcoholysis, provided the changes of rotation due to the direct action of the catalyst on the ester or on the products of alcoholysis are absent or compensated. No appreciable direct effect was found in the case of the alcoholysis reactions 1 to 4 for concentrations of the catalyst up to 0.5 *N*.

In a mixture of menthol with 10% of benzene and 0.6930 *N* hydrogen chloride in a 2-dm. tube at 30°, there was no change in the optical rotation in the course of 15 days.

Further, evidence cited below in the section headed "Strength of Catalyst" shows that the change in strength of catalyst observed for 35 days was practically the same for the following mixtures at the same temperature: (*a*) methyl alcohol + hydrogen chloride (about 0.5 *N*); (*b*) methyl alcohol + hydrogen chloride as in (*a*) + menthyl crotonate (the ratio of the crotonate to alcohol is about the same as in the alcoholysis mixtures); (*c*) methyl alcohol + hydrogen chloride as in (*a*) + menthol, an amount equivalent to that of the menthyl crotonate used in (*b*).

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

When, however, the concentration of the catalyst is considerably increased, the direct action becomes pronounced. Table II gives the rotation of two solutions of menthol with 10% benzene, for 1.27 *N* and 2.55 *N* hydrogen chloride, respectively.

TABLE II

ROTATION OF MENTHOL WITH DIFFERENT CONCENTRATIONS OF HYDROGEN CHLORIDE

Days from start	0	1	6	12	35
Rotation, 1.27 *N* HCl[a]	−85.59	−85.59	....	−85.56	−85.36
2.55 *N* HCl[a]	−87.84	−87.62	−87.56	−87.49	−86.73

[a] Gas.

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

Strength of Catalyst

Expt. 1 (*a*) with menthyl butyrate, methyl alcohol and 0.02434 *N* hydrogen chloride, showed that the reaction was very slow; in subsequent experiments, therefore, 1 (*b*) and 1 (*c*), the concentrations of the catalyst were increased 10 to 15 times. When, however, in Expts. 2 and 4 it was found desirable to use still higher concentrations, as the reactions were very much slower, and as the direct action of hydrogen chloride on the methyl alcohol was pronounced, it was necessary to determine the nature and extent of this change.

Changes in the strength of catalyst in the following three mixtures have been determined by titrating from time to time 2 cc. of the mixtures with standard 0.5348 *N* sodium hydroxide solution drawn from a 10 cc. buret graduated to read to 0.02 cc. In Expts. *a* and *b* a mixture of methyl alcohol and 0.5 *N* hydrogen chloride was used together with as much methyl crotonate as is employed in an actual experiment for alcoholysis, namely, 1 molecular equivalent of ester for about 40 of the alcohol.

In Expt. *c* a mixture of methyl alcohol and 0.5 *N* hydrogen chloride (as in the above) was used, together with 1 molecular equivalent of menthol to 40 of alcohol.

TABLE III

CHANGES IN STRENGTH OF CATALYST

Days from start	0	1	6	12	35
Titration,[a] Expt. *a*	1.715	1.680	1.445	1.240	0.930
Expt. *b*	1.715	1.680	1.425	1.100	.85
Expt. *c*	1.715	1.690	1.410	1.210	.86

[a] In cc. for each 2 cc. of test solution.

It is obvious from the above that the change in the three cases is approximately the same. One can assume that the change in all the cases is due to the direct action of hydrogen chloride on the methyl alcohol, and that, as already remarked, direct action of hydrogen chloride on the ester or on the menthol is negligible.

Calculation of Results

The reactions studied have been of the following types.

I. A unimolecular alcoholysis reaction; the strength of the catalyst remains unchanged during the reaction as the reaction proceeds rapidly. Reactions 1 and 3 are of this nature. In Reaction 7, namely ethyl butyrate + menthol ⟶ menthyl butyrate + ethyl alcohol, although the reaction is slow, the strength of catalyst remains constant, as the catalyst has practically no direct action on the menthol or on the ethyl alcohol formed during the course of the reaction.

II. A unimolecular alcoholysis reaction accompanied by an independent change in strength of catalyst brought about by the direct action of the catalyst on the reacting alcohol as such, or on any impurity (water vapor) that may be present or on both, resulting in a gradual diminution of the velocity constant. Reactions 2 and 4, the alcoholysis of menthyl crotonate and cinnamate with methyl alcohol, are of this nature.

III. A unimolecular alcoholysis reaction accompanied by a side reaction bringing about a change in strength of the catalyst proportional to the extent to which the alcoholysis has proceeded. Reaction 5 is an example: methyl butyrate + menthol ⟶ menthyl butyrate + methyl alcohol.

Hydrogen chloride has no action on the menthol so long as the strength of acid is not greater than 0.5 N; but it acts strongly on the methyl alcohol as the latter is being formed, resulting in a continuous decrease in the strength of acid in the mixture and a corresponding decrease in the velocity constant.

IV. When the strength of catalyst exceeds 0.5 N, hydrogen chloride begins to act on the menthol, resulting in 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 6 is an example of this type.

Reactions of Type I.—For calculating the velocity constant in reactions of Type I the formula derived in a previous paper[12] has been used.

$$k = \frac{1}{C} \frac{1}{T_{3\cdot2} - T_{2\cdot1}} \ln \frac{x_{2\cdot1}}{x_{3\cdot2}} \tag{1}$$

k is the velocity constant; $x_{2\cdot1}$, $x_{3\cdot2}$.... are rates of change at times $T_{2\cdot1}$, $T_{3\cdot2}$...., 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 $x_{2\cdot1}$, $x_{3\cdot2}$.... are plotted against $T_{2\cdot1}$, $T_{3\cdot2}$, ...; the line passing through the several points makes with the axis of time an angle whose tangent is k, corresponding to the strength of catalyst C. As k is directly proportional to the strength of catalyst, so k corresponding to N hydrogen chloride as catalyst has been calculated.

Reactions of Type II.—Here the change in the strength of the catalyst is about 12%, depending on the time during which the reaction has been proceeding. As the change is independent of the main reaction, we can write,

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

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

Where a is the amount of ester in the mixture, at the beginning of the reaction, y is the change in the strength of catalyst, at time t, and k and k' are constants.

---

[12] Ref. 1, p. 188.

Dividing (2) by (3),

$$\frac{\mathrm{d}x}{\mathrm{d}y} = (a - x)\frac{k}{k'} \tag{4}$$

On integrating and substituting the value of y in (2) we obtain

$$k = \frac{1}{C}\left(\frac{1}{(a - x)}\frac{\mathrm{d}x}{\mathrm{d}t} - k' \; ln \; \frac{a - x}{a}\right) \tag{4}$$

In this equation, all factors except k, k' can be obtained directly from the optical rotations of the mixture during the reaction, and from the known values of the initial amount of the ester and concentration of the catalyst. Substituting two sets of these values in Equation 4, k, the velocity constant of the reaction, can be obtained.

Reactions of Type III.—Since 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

$$\frac{\mathrm{d}y}{\mathrm{d}t} = k' \, x \, (C - y) \tag{5}$$

On dividing Equation 2 by 5, we obtain

$$\frac{\mathrm{d}x}{\mathrm{d}y} = \frac{k}{k'}\,\frac{a - x}{x} \tag{6}$$

This is integrated and the value of y substituted in (2).

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k \; (a - x)\left(C + \frac{k'}{k}x + a \; ln \; \frac{a - x}{a}\right)$$

$$k = \frac{1}{C}\left(\frac{1}{a - x}\frac{\mathrm{d}x}{\mathrm{d}t} - k' \, x \; - \; k'a \; ln \; \frac{a - x}{a}\right) \tag{7}$$

Equation 4 differs essentially from Equation 1 only by the term, $-k'$ log $\frac{a-x}{a}$; while (7) has in addition, a, multiplying this term, and has, further, a term $-k'x$. These new Equations, 4 and 7, hold fairly well for the reactions studied.

In Tables I to V the symbols used have the following meanings.

D: the date on which the observation of the optical rotations of the alcoholysis mixture was begun.

R: the ratio of the molecules of alcohol to those of 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: the concentration of hydrochloric acid in the alcoholysis mixture at the 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: the rotation in degrees of the alcoholysis mixture contained in a 2-dm. tube.

x: the change in grams of the amount *a* of ester due to alcoholysis in a time counted from the moment the alcoholysis mixture was made.

t: the time, in minutes.

T: the 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. This occurs only in the tabulation of the results of Reactions I, III and VII.

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

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

Experimental Results

Experimental figures are given for typical cases. The values of *k* in the several experiments have been tabulated.

TABLE IV

REACTION 1. MENTHYL BUTYRATE AND METHYL ALCOHOL

(2) *D*:18.2–21 $R = 42$ $C = 2238\ N - (0.2220\ N)$

t	r	dr	dt	T	$\text{Log}\ \frac{\text{d}r}{\text{d}t}$
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	.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	$\bar{3}.122$

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

TABLE V

REACTION 2. MENTHYL CROTONATE AND METHYL ALCOHOL

(1) *D*: 2–3–21 $R = 45$ $C = 0.4717\ N - (0.4135\ N)$

t	r	$-\text{d}r$	$-0.2025\ \text{d}r = x$	$a-x$	$-\frac{\text{d}(a-x)}{\text{d}t} \times 10^4$	$-\frac{10^4}{a-x} \times \frac{\text{d}}{\text{d}t}(a-x)$	$-\log \frac{a-x}{a}$	$k \times 10^4$
0	18.22	0	0	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	.496	1.669	4.07	2.44	.113	5.64 (1000, 2000)
1500	14.86	3.36	.680	1.485	...	...	...	.....
2000	14.06	4.16	.842	1.323	2.96	2.24	.213	5.38 (2000, 4000)
2500	13.40	4.82	.976	1.189	...	...	...	.....
3000	12.82	5.40	1.092	1.072	2.19	2.04	.304	5.67 (1000, 3000)
3500	12.32	5.90	1.195	0.970	...	...	...	.....
4000	11.87	6.35	1.285	.880	1.75	1.99	.390	5.56 (1000, 4000)
4500	11.47	6.75	1.370	.795	...	...	...	.....

$k = 5.62 . 10^{-4}$

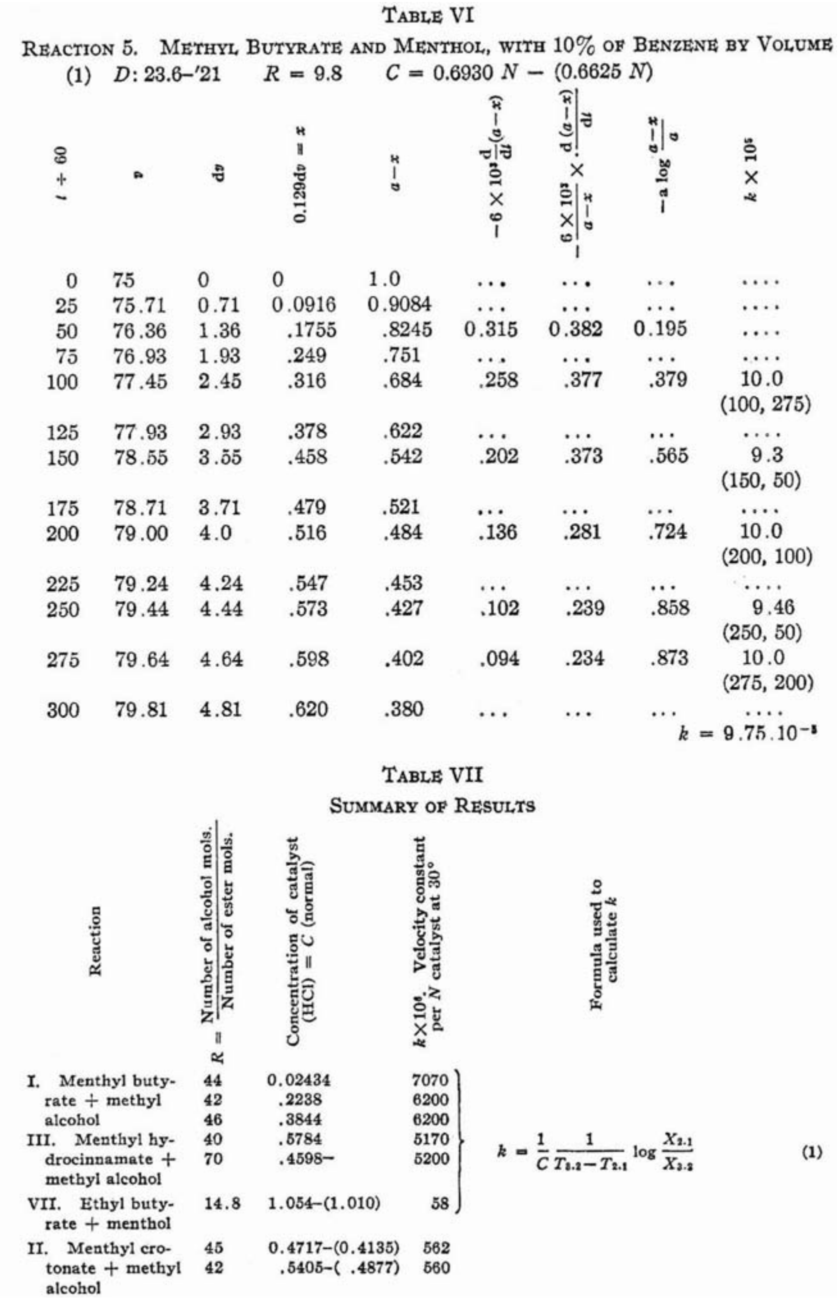

TABLE VI

REACTION 5. METHYL BUTYRATE AND MENTHOL, WITH 10% OF BENZENE BY VOLUME

(1) D: 23.6–'21 $R = 9.8$ $C = 0.6930\ N - (0.6625\ N)$

$t \div 60$	v	dv	$0.129dv = x$	$a - x$	$-6 \times 10^3 \frac{d}{dt}(a-x)$	$-\frac{6 \times 10^3}{a-x} \times \frac{d(a-x)}{dt}$	$-a \log \frac{a-x}{a}$	$k \times 10^5$
0	75	0	0	1.0	...	...	...	....
25	75.71	0.71	0.0916	0.9084	...	...	...	....
50	76.36	1.36	.1755	.8245	0.315	0.382	0.195	....
75	76.93	1.93	.249	.751	...	...	...	....
100	77.45	2.45	.316	.684	.258	.377	.379	10.0 (100, 275)
125	77.93	2.93	.378	.622	...	...	...	....
150	78.55	3.55	.458	.542	.202	.373	.565	9.3 (150, 50)
175	78.71	3.71	.479	.521	...	...	...	....
200	79.00	4.0	.516	.484	.136	.281	.724	10.0 (200, 100)
225	79.24	4.24	.547	.453	...	...	...	....
250	79.44	4.44	.573	.427	.102	.239	.858	9.46 (250, 50)
275	79.64	4.64	.598	.402	.094	.234	.873	10.0 (275, 200)
300	79.81	4.81	.620	.380	...	...	...	....

$k = 9.75 . 10^{-5}$

TABLE VII

SUMMARY OF RESULTS

Reaction	$R = \frac{\text{Number of alcohol mols.}}{\text{Number of ester mols.}}$	Concentration of catalyst (HCl) = C (normal)	$k \times 10^6$. Velocity constant per N catalyst at 30°	Formula used to calculate k	
I. Menthyl butyrate + methyl alcohol	44	0.02434	7070	$k = \frac{1}{C} \frac{1}{T_{3.2} - T_{2.1}} \log \frac{X_{2.1}}{X_{3.2}}$	(1)
	42	.2238	6200		
	46	.3844	6200		
III. Menthyl hydrocinnamate + methyl alcohol	40	.5784	5170		
	70	.4598–	5200		
VII. Ethyl butyrate + menthol	14.8	1.054–(1.010)	58		
II. Menthyl crotonate + methyl alcohol	45	0.4717–(0.4135)	562		
	42	.5405–(.4877)	560		

TABLE VII (*Concluded*)

Reaction	$R = \frac{\text{Number of Alcohol Mols.}}{\text{Number of ester mols.}}$	Concentration of catalyst (HCl) = C (normal)	$k \times 10^6$, Velocity constant per N catalyst at 30°	Formula used to calculate k
IV. Menthyl cinnamate + methyl alcohol	44	.5480–(.4852)	385	$k = \frac{1}{C}\left\{\frac{1}{a-x}\frac{dx}{dt} - k' \log \frac{a-x}{a}\right\}$ (4)
	47	.4088–(.3714)	405	
	52[a]	.5832–(.5280)	393	
	52	.5832–(.5280)	404	
V. Methyl butyrate + menthol	9.8[b]	.6930–(.6625)	97.5	
	10.0[b]	1.010 –(.9583)	91.3	
VI. Methyl crotonate + menthol	13.0[b]	1.010 –(.832)	9.72	$k = \frac{1}{C}\left\{\frac{1}{a-x}\frac{dx}{dt} - k'x - k'a \log \frac{a-x}{a}\right\}$ (7)

[a] In this experiment 10% of benzene was added to the mixture to show that it has no influence on alcoholysis.

[b] In these experiments 10% of benzene was added to the menthol so as to keep the alcoholysis mixture liquid.

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

TABLE VIII

VELOCITY CONSTANTS

Initial ester mixture		Alcoholysis constant for N HCl at 30° $k \times 10^6$
Menthyl butyrate	+ methyl alcohol	6200
Menthyl crotonate	+ methyl alcohol	561
Menthyl hydrocinnamate	+ methyl alcohol	5185
Menthyl cinnamate	+ methyl alcohol	397
Ethyl butyrate	+ methyl alcohol	90200
Ethyl crotonate	+ methyl alcohol	6250
Ethyl hydrocinnamate	+ methyl alcohol	78000
Ethyl cinnamate	+ methyl alcohol	3900
Ethyl butyrate	+ menthol	58
Methyl butyrate	+ menthol	94.4
Methyl crotonate	+ menthol	9.7
Methyl butyrate	+ ethyl alcohol	19800
Methyl crotonate	+ ethyl alcohol	1400
Methyl hydrocinnamate	+ ethyl alcohol	19100
Methyl cinnamate	+ ethyl alcohol	1075

Discussion of Results

1. An α,β-olefinic linkage in the acyl group in an ester exerts a strong retarding influence in the alcoholysis of the ester. This is illustrated in Table IX.

TABLE IX

RETARDATION OF ALCOHOLYSIS

Velocity constant		Alcoholysis	Esterification	Hydrolysis
$\frac{k \text{ (menthyl butyrate, methyl alc.)}}{k \text{ (menthyl crotonate, methyl alc.)}}$	=	11.05	..	..
$\frac{k \text{ (menthyl hydrocinnamate, methyl alc.)}}{k \text{ (menthyl cinnamate, methyl alc.)}}$	=	13.05	..	..
$\frac{k \text{ (methyl butyrate, menthol)}}{k \text{ (methyl crotonate, menthol)}}$	=	9.73	..	..
$\frac{k \text{ (ethyl butyrate, methyl alc.)}}{k \text{ (ethyl crotonate, methyl alc.)}}$	=	14.5	..	29[c]
$\frac{k \text{ (ethyl hydrocinnamate, methyl alc.)}}{k \text{ (ethyl cinnamate, methyl alc.}}$	=	20	36.0[a]	30[c]
$\frac{k \text{ (methyl butyrate, ethyl alc.)}}{k \text{ (methyl crotonate, ethyl alc.)}}$	=	13.6	39.0[b]	..
$\frac{k \text{ (methyl hydrocinnamate, ethyl alc.)}}{k \text{ (methyl cinnamate, ethyl alc.)}}$	=	17.8	50.5[b]	..
	Mean	14.2	41.8	29.5

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

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

[c] Sudborough and Williams, *ibid.*, **101**, 412 (1912).

The retardation, as can be seen, is of the same order, the mean value being 14.2. Similar retardation in esterification and hydrolysis are also given, for comparison, in cases where the velocity constant is known, the mean values being 41.8 and 29.5, respectively. The retardation, in alcoholysis, is less than the average with menthyl esters, or when menthol has been used.

2. Further, this retardation is decidedly more when the esters have a heavy phenyl group replacing the β-methyl. Thus,

$$(a)\quad \frac{k \text{ menth. hydrocinn., MeOH}}{k \text{ menth. cinn., MeOH}} \quad \frac{k \text{ menth. butyr., MeOH}}{k \text{ menth. crot., MeOH}} = \frac{13.05}{11.05} = 1.18$$

$$(b)\quad \frac{k \text{ Et hydrocinn., MeOH}}{k \text{ Et cinn., MeOH}} \quad \frac{k \text{ Et butyr., MeOH}}{k \text{ Et crot., MeOH}} = \frac{20.0}{14.5} = 1.38$$

$$(c)\quad \frac{k \text{ Me hydrocinn., EtOH}}{k \text{ Me cinn., EtOH}} \quad \frac{k \text{ Me butyr., EtOH}}{k \text{ Me crot., EtOH}} = \frac{17.8}{13.6} = 1.31$$

The meanings of the symbols are as follows: Et, ethyl; Me, methyl; EtOH, ethyl alcohol; MeOH, methyl alcohol.

3. In Paragraph 2, while (*c*) and (*b*) are nearly equal, (*a*) is decidedly smaller, showing that the alkyl group in the substituted carboxyl of the ester has an opposing polarity to that of the group attached to the carbon in the beta position to the carboxyl. Thus while the ethyl group of the substituted carboxyl in (*b*) and the methyl group in (*c*) are not able to suppress

the individuality of the phenyl group, the heavy menthyl group in (*a*) has achieved it, as shown by the approach of the ratio to 1.

4. Substitution of a phenyl group for a methyl attached to a beta carbon atom lowers the velocity constant:

$$(a)\quad \frac{k\text{ menthyl butyrate, methyl alc.}}{k\text{ menthyl hydrocinnamate, methyl alc.}} = 1.19$$

$$(b)\quad \frac{k\text{ menthyl crotonate, methyl alc.}}{k\text{ menthyl cinnamate, methyl alc.}} = 1.68$$

$$(c)\quad \frac{k\text{ ethyl butyrate, methyl alc.}}{k\text{ ethyl hydrocinnamate, methyl alc.}} = 1.16$$

$$(d)\quad \frac{k\text{ ethyl crotonate, methyl alc.}}{k\text{ ethyl cinnamate, methyl alc.}} = 1.60$$

$$(e)\quad \frac{k\text{ methyl butyrate, ethyl alc.}}{k\text{ methyl hydrocinnamate, ethyl alc.}} = 1.04$$

$$(f)\quad \frac{k\text{ methyl crotonate, ethyl alc.}}{k\text{ methyl cinnamate, ethyl alc.}} = 1.30$$

5. In Paragraph 4, the ratios are: $b > a$; $d > c$; $f > e$. This shows that the influence of the group attached to the beta carbon atom, is more pronounced when there is a double linkage in the α,β position. It is probable that the double linkage brings the groups nearer to one another, so that their relative retarding influences become more pronounced, in proportion to their masses.

6. The influence of the alkyl groups in the substituted carboxyl, with the alcohols remaining the same is as follows.

$$(a)\quad \frac{k\text{ ethyl butyrate, methyl alc.}}{k\text{ menthyl butyrate, methyl alc.}} = 14.6$$

$$(b)\quad \frac{k\text{ ethyl crotonate, methyl alc.}}{k\text{ menthyl crotonate, methyl alc.}} = 11.2$$

$$(c)\quad \frac{k\text{ ethyl hydrocinnamate, methyl alc.}}{k\text{ menthyl hydrocinnamate, methyl alc.}} = 15.0$$

$$(d)\quad \frac{k\text{ ethyl cinnamate, methyl alc.}}{k\text{ menthyl cinnamate, methyl alc.}} = 9.85$$

$$(e)\quad \frac{k\text{ methyl butyrate, menthol}}{k\text{ ethyl butyrate, menthol}} = 1.625$$

The ratio of *a* to *b* is 1.3 : 1; and that of *c* to *d* is 1.5 : 1. That *b* is less than *a* and *d* less than *c* can be explained as follows.

In Paragraph 3 it has been shown that the group in the substituted carboxyl and the alkyl attached to the carbon in the beta position to the substituted carboxyl have opposite polarities; that is, their influences tend to counteract each other, although an increase in weight of either increases the retardation of the alcoholysis. In Paragraph 5 it has been shown that a double linkage may perhaps be looked upon as bringing the groups nearer to each other, in which case the counteracting force becomes stronger and the reaction will become a little accelerated. Thus, both the numerator and denominator in (*b*) and (*d*) under Paragraph 6 will be increased. However, the heavier menthyl group is in the denominators and their percentage increase is therefore greater than that of the numerators, with the result that the values of the ratios diminish, more than in (*a*) and (*c*).

It is obvious that by an increase in the weight of the alkyl group in the substituted carboxyl the retardation is increased, but how this retardation is to be compared with the weights of the alkyl groups, is not clear.

7. The ratio of the constants for the direct and the reverse reaction is independent of the nature of the acids, as was shown by Kolhatkar.[3]

For the interchanging of menthyl and methyl groups, the ratios are as follows.

$$(a)\quad \frac{k\text{ menthyl butyrate, methyl alcohol}}{k\text{ methyl butyrate, menthol}} = 65.7$$

$$(b)\quad \frac{k\text{ menthyl crotonate, methyl alc.}}{k\text{ methyl crotonate, menthol}} = 58.0$$

$$\text{Mean}\quad 62.0$$

For the interchanging of methyl and ethyl groups, the ratios are as follows.

$$(c)\quad \frac{k\text{ ethyl butyrate, methyl alc.}}{k\text{ methyl butyrate, ethyl alc.}} = 4.6$$

$$(d)\quad \frac{k\text{ ethyl crotonate, methyl alc.}}{k\text{ methyl crotonate, ethyl alc.}} = 4.4$$

$$(e)\quad \frac{k\text{ ethyl hydrocinnamate, methyl alc.}}{k\text{ methyl hydrocinnamate, ethyl alc.}} = 4.1$$

$$(f)\quad \frac{k\text{ ethyl cinnamate, methyl alc.}}{k\text{ methyl cinnamate, ethyl alc.}} = 3.6$$

$$\text{Mean}\quad 4.2$$

In conclusion I wish to thank Dr. Sudborough for suggesting the work and for valuable suggestions in connection with its prosecution. The experimental part was carried out in the Laboratories of the Indian Institute of Science, at Bangalore, and my obligations are further due to the Institute for the grant of a scholarship which enabled me to accomplish it. My thanks are also due to Professor K. F. Herzfeld of the University of Munich for valuable suggestions.

Summary

Velocity constants, *k*, in alcoholysis reactions, involving the interchange of alkyl radicals when an ester and an alcohol react in presence of dry hydrogen chloride as catalyst at 30°, have been determined from observations on the change in optical rotations of the reacting mixtures for the following substances: menthyl esters of crotonic and cinnamic acids with unsaturation in the α,β position to the carboxyl group and of their corresponding saturated analogs, with absolute methyl alcohol in large excess; for the reverse reactions with methyl esters of crotonic and butyric

acids using menthol in large excess; and lastly, for ethyl butyrate with menthyl. These velocity constants are directly proportional to the strength of the catalyst. For N hydrochloric acid $k \times 10^6$ has the following values: 561, 397, 6200, 5185, 9.7, 94.4 and 58, respectively. With these are tabulated the values for the ethyl esters of the same acids, in the presence of an excess of absolute methyl alcohol and for the reverse reactions, calculated from data given in a previous paper.[1] The constants so obtained are, 6250, 3900, 90,200, 78,000, 1400, 1075, 19,800 and 19,100, respectively. From these values the following conclusions have been drawn. (1) An olefinic linkage in the acyl group exerts a retarding effect in alcoholysis comparable with the effect in esterification and hydrolysis; these effects are on the average, 14.2, 41.8 and 29.5, respectively. (2) This retardation is on an average 1.35 times greater when the esters have a phenyl group replacing a methyl, but is appreciably smaller with menthyl esters. (3) The alkyl group in the substituted carboxyl radical of the ester has a polarity opposed to that of the alkyl group attached to the carbon in the beta position to the carboxyl group. (4) Replacement of the methyl of the beta carbon by a phenyl group lowers the velocity constant, in the ratio of 1.3:1 when there is an olefinic linkage, but 1.5:1 when the molecule is saturated. (5) Double linkage perhaps brings the alkyl attached to the beta carbon nearer to the carboxyl group, where its influence is more pronounced. (6) Methyl alcohol reacts 13 times more rapidly with the ethyl esters than with menthyl esters. Menthol reacts 1.6 times more rapidly with methyl than with ethyl esters. (7) The ratio of the constants of the direct and the reverse reactions depends only on the nature of the interchanging groups but not appreciably on the nature of the acids. It is 62 or 4.2 according as menthyl and methyl, or ethyl and methyl groups are interchanged.

A fuller account of this work will appear in the *Journal of the Indian Institute of Science*, Bangalore, India.

MUNICH, GERMANY