THE VELOCITY OF ALCOHOLYSIS OF ESTERS OF DIBASIC ACIDS.

By Z. H. Patel and H. E. Watson

The velocity of alcoholysis of several esters of monobasic acids has been measured by Kolhatkar (*J.C.S.*, 1915, **107**, 921) and by Dasannacharya and Sudborough (*J. Indian Inst. Sci.*, 1921, **4**, 81; 1924, **7**, 1) but no corresponding observations appear to have been made with esters of dibasic acids, although the interchange of radicals has been demonstrated. Leuchs and Theodoresen (*Ber.*, 1910, **43**, 1239) examined the conversion of diethyl malonate into the methyl ester in presence of ammonia; Bruni and Contardi (*Atti R. Accad. Lincei*, 1906, V, **15**, 637; Gazzetta, 1906, **36**, 356) showed by polarimetric measurements that menthol reacts with ethyl oxalate and malonate with appreciable velocity at 100°, while Pfannl (*Monatsh.*, 1910, **31**, 307) taking advantage of the insolubility of certain esters showed that the rate of interchange of methyl, ethyl and propyl radicals in the esters of terephthalic, benzoic and oxalic acids was approximately proportional to the amount of alkali added as a catalyst.

In the case of an ester with two replaceable groups, the question arises whether both groups are replaced simultaneously or successively and in the latter case whether the velocity of alcoholysis of each group is the same. A reaction in which two alkyl groups simultaneously react with one molecule of an ester is most improbable, while the formation of an intermediate compound has been proved definitely by Sudborough and Bhagvat for the case of methyl oxalate and *iso*butyl alcohol (*J. Indian Inst. Sci.*, 1920, **2**, 121). It thus seems certain that the reaction takes place in two stages. If this is so, it is evident that in the most general case four reactions occur. Consider the action between ethyl alcohol and the ester $COOMe.R_1......R_2\,COOMe$. Either of the methyl groups may react giving rise to the compounds $COOEt.R_1......R_2.COOMe$ and $COOMe.R_1......R_2.COOEt$, each of which can react with another molecule of ethyl alcohol. The equation representing the velocity of these reactions is one of some complexity but it becomes very much simplified if it is assumed that the substitution of Me by Et in the grouping attached to R_2 does not alter the rate of reaction of the other Me group, or in other words, if the velocity of esterification of the Me group adjacent to R_1 in the esters $COOMe.R_1...R_2.COOMe$ and $COOMe.R_1....R_2.COOEt$ is the same. With this assumption the case becomes that of the esterification of a mixture of the esters R_3.COOMe and R_4.COOMe in equimolecular proportion. If a large excess of alcohol is used, both reactions may be regarded as unimolecular and the following equations hold good.

$$a - x_1 = ae^{-K_1 t} \qquad a - x_2 = ae^{-K_2 t} \tag{1}$$

where x_1 x_2 are the concentrations of ester formed after time t, a is the initial concentration and K_1 K_2 are the velocity coefficients. Corresponding with every molecule esterified there will be a definite volume change. If this is assumed to be constant so that the total volume change is proportional to x, putting $x = bv$ and $a = bV$ where V is the volume change when the reaction is complete,

$$V_1 - v_1 = V_1\, e^{-K_1 t} \text{ and } V_2 - v_2 = V_2\, e^{-K_2 t} \tag{2}$$

The total volume change at time t is—

$$v_1 + v_2 = V_1\,(1 - e^{-K_1 t}) + V_2\,(1 - e^{-K_2 t})$$

No data are available for determining V_1 and V_2, but if they are equal

$$v/V = 1 - \tfrac{1}{2}\,(e^{-K_1 t} + e^{-K_2 t}) \tag{3}$$

In the case of a symmetrical ester $K_1 = K_2$ and $v/V = 1 - e^{-Kt}$ or

$$\ln\,(1 - v/V) = Kt \tag{4}$$

the usual equation for a unimolecular reaction.

The reaction velocity for several methyl and ethyl esters of dibasic acids in presence of hydrochloric acid has now been measured by a dilatometric method and the velocity coefficients calculated by means of equations (3) and (4). The extent to which the assumptions made in deducing these equations are justified may be seen from the results which follow.

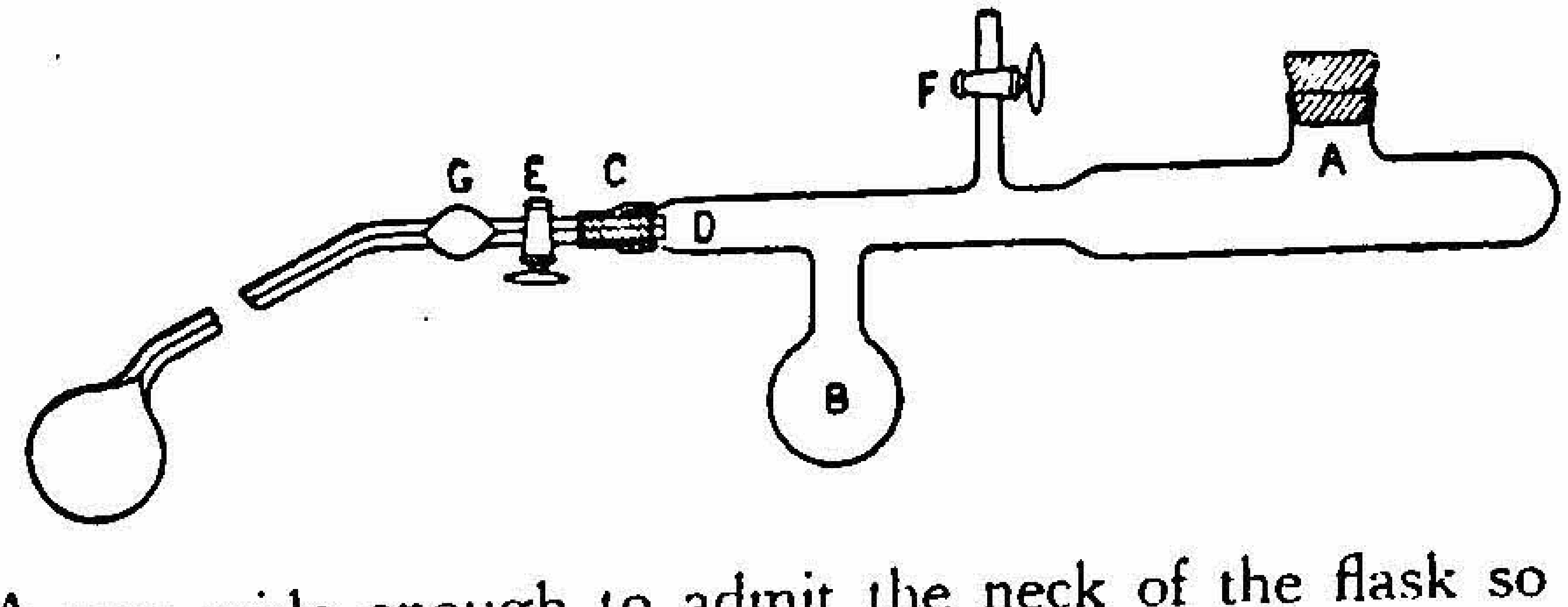
EXPERIMENTAL

Preparation of esters.—The esters were prepared by refluxing the acids with 5 molecular proportions of absolute alcohol containing 3 to 4 per cent of hydrochloric or sulphuric acid, except in the case of oxalic acid for which no catalyst was required. After separation and neutralisation they were dried with anhydrous magnesium sulphate and fractionated under reduced pressure. All boiled within a range of 1° and the physical constants agreed with those given in the literature. Methyl azelate which does not appear to have been prepared previously was made from a pure specimen of azelaic acid; it boiled at 175° (unc.) /38mm, Methyl and ethyl alcohols after preliminary drying were treated 3 times with metallic calcium and fractionated. Their densities showed that they contained less than 0.03 per cent of water. They were stored in Jena glass bottles with syphon delivery tubes connected to burettes and protected from moisture by means of soda lime and phosphorus pentoxide.

Preparation of the reaction mixtures.—The presence of water even in small quantities is known to exert a very great influence upon reactions involving alcoholysis. No actual measurements were made with esters of dibasic acids, but it has been found during the course of analogous experiments not yet published that the addition of 1 per cent. of water reduces the velocity coefficient of alcoholysis of methyl propionate by 60 per cent. It was necessary therefore to take very great care not to expose the solutions to the atmosphere at any time. This was effected by running the necessary quantity of absolute alcohol from its burette into a Jena glass bottle filled with dry air and fitted with a two-holed cork to which a drying tube was attached. The tip of the burette was withdrawn from the second hole and a glass tube inserted, through which dry hydrogen chloride from fused ammonium chloride and sulphuric acid could be passed into the alcohol. By counting the bubbles of gas in a sulphuric acid bubbler it was possible to prepare a solution of suitable strength which was approximately double the concentration used for alcoholysis. A sample of the acid solution was withdrawn and the exact strength found by titration. The remaining solution was then syphoned into a dry burette and the required quantity run into a 50 c.c. graduated flask containing a measured quantity (2-3 c.c.) of ester protected from moist air and the mixture diluted to 50 c.c. with alcohol.

To fill the dilatometer, the flask after shaking was emptied into the special apparatus (shown in fig. I) previously filled with dry air. The

Fig. I



T-tube A was wide enough to admit the neck of the flask so that no contamination occurred during pouring. A was then corked and all the liquid run into the bulb B. The evacuated dilatometer was then inserted through the small rubber tube C which up to this stage had been closed with a glass rod. The liquid was poured into the lower portion D of the filler and the dilatometer filled as much as possible by opening the tap E. Removal of the last bubbles of air was effected by evacuation of the apparatus through the tap F and readmission of dry air. The bulb G greatly facilitated the filling operation which could be carried out very quickly in practice. The final adjustment of the liquid in the capillary to a suitable level was made in the thermostat. A trial experiment made by breaking a dilatometer bulb and titrating the contents, showed that the concentration of acid was unchanged by this process of filling.

The dilatometers had a volume of about 40 c.c. and the capillaries, bent as recommended by Kolhatkar (*loc. cit.*) to facilitate clamping, had a cross section of 0.0012 to 0.0018 sq. cm. The bore and uniformity were measured by weighing threads of mercury. All experiments were made in a thermostat at 30° but as a difference of temperature of 0.01° caused a movement of the meniscus of 3 mm., a second bulb containing alcohol and acid but no ester was used as a blank to allow for small temperature variations and also for small changes in volume which might occur owing to the action of the acid on the alcohol when methyl alcohol was used. The dilatometer tap was kept closed except during a reading when it was opened to equalise the pressure, and the position of the meniscus was ascertained by measuring its distance from a fixed mark on the dilatometer stem with a cathetometer.

RESULTS

In Table I detailed readings for one experiment are given in order to illustrate the method of calculation. Since the ester was symmetrical, the velocity coefficients K were calculated by means of equation (4) and the results were constant to the limit of experimental error. The total change in volume has been assumed to be the change corresponding with the completion of the reaction. Strictly speaking it corresponds with the equilibrium point, but with the large excess of alcohol used the correction to K is small, amounting in the present case to about 2.8 per cent. The application of this correction is discussed in greater detail on p. 64. The dilatometer readings were corrected for variations in the volume of liquid in the bulb used as a blank by adding or subtracting the observed change (in mm.) multiplied by a factor, 0.8, which allowed for the difference in volumes of the bulbs and capillaries. In most cases experiments were conducted with two different strengths of acid and the results were reduced to the value for $0.05N$ acid assuming that the velocity coefficients were proportional to the concentration of catalyst.

TABLE I

Dimethyl azelate and ethyl alcohol

Volume of dilatometer 42.5 c.c. ; capillary 0.00175 c.c./cm.
Volume of dilatometer for blank 42.0 c.c. ; capillary 0.00140 c.c./cm.
Conc. of HCl 0.1046*N*.—Ester 1.3 g. in 50 c.c. or 138 : 1 mols.

Time mins.	Change in blank, mm.	Change in reaction capillary, mm.	Corrected change	$K \times 10^5$
37	−0.2	3.2	3.05	246
75.5	−1.0	6.5	5.7	237
100	−1.4	8.7	7.6	246
150	−0.3	10.9	10.65	244
209	−0.4	14.5	14.2	251
274	−1.1	17.8	16.9	242
330	−0.7	19.7	19.15	242
458	−5.2	27.5	23.35	242
1200	−3.3	35.2	32.55	...
1430	0.8	32.9	33.55	...
1470	2.0	32.9	34.5	...
1780	0.9	34.1	34.8	...
2500	−2.7	37.0	34.85	...
∞	...	...	34.85	...
...	...	...	...	mean 244

$K \times 10^{-5}$ for 0.50*N*. acid = 117

In Table II further results are given in an abbreviated form. *N* denotes the normality of the acid, *C* the weight or volume of ester in 50 c.c., *t* the time of reaction in minutes, *x* the total movement of the meniscus in the dilatometer tube (corrected) in mm., k, $K \times 10^5$ and k' $K \times 10^5$ for 0.05 *N* acid,

TABLE II

Dimethyl oxalate, ethyl alcohol.

$N=0.0267$ $C=2.303$g.			$N=0.1004$ $C=2.685$g.		
t	x	k	t	x	k
81	10.7	141	65	27.5	504
157	20.2	144	84	34.1	504
232	28.5	145	109	42.4	506
298	35.0	145	135	49.5	515
356	40.1	145	183	60.6	522
464	49.0	146	263	73.6	520
576	55.8	143	327	81.0	529
1281	84.3	146	384	85.8	534
∞	99.6	...	∞	98.5	...

$k_m=144$ $k'=270$ $k_m=518$ $k'=258$

Diethyl oxalate, methyl alcohol.

$N=0.0264$ $C=2.0$c.c.			$N=0.0525$ $C=2.5$c.c.		
t	x	k	t	x	k
34	10.7	421	16	11.0	849
58	17.2	416	27	17.1	815
98	26.7	414	44	26.3	821
138	34.6	410	63	34.9	819
207	44.5	403	108	50.3	805
298	55.2	391	145	59.3	796
357	60.4	393	188	67.2	796
∞	80.1	...	214	70.6	788
...	...	...	∞	86.6	...

$k_m=407$ $k'=771$ $k_m=800$ $k'=762$

Dimethyl malonate, ethyl alcohol.

$N=0.0977$ $C=2.05$c.c.			$N=0.1876$ $C=2.05$c.c.		
t	x	k	t	x	k
142	13.6	78.7	60	11.2	152
222	21.2	81.2	131	23.9	158
285	26.7	81.7	180	31.1	154
442	39.5	83.0	245	40.8	157
555	47.8	84.0	307	48.8	156
614	51.4	83.0	399	51.5	157
1276	83.4	82.0	∞	128.1	...
1435	89.3	81.0	...	...	...
1649	95.1	81.7	...	...	...
1990	102.4	80.0	...	...	...
∞	128.5	...	...	...	...

$k_m=81.6$ $k'=41.9$ $k_m=156$ $k'=41.4$

Diethyl malonate, methyl alcohol.

$N=0.0522$ $C=2.6$ c.c.			$N=0.0523$ $C=2.6$c.c.		
t	x	k	t	x	k
30.5	6.7	151	29	6.4	155
54.5	11.8	151	76	15.9	151
90	18.4	146	133	26.7	151
150	29.0	144	214	41.0	153
221	40.8	144	291	52.2	152
306	53.1	143	328	57.0	150
406	66.1	143	489	76.0	149
672	92.2	142	1214	123.5	151
1308	128.5	150	∞	146.8	...
1406	131.2	150	...	...	...
∞	149.8	...	...	...	...

$k_m=146$ $k'=140$ $k_m=151$ $k'=144$

Dimethyl succinate, ethyl alcohol

$N=0.0494$ $C=2.3$ c.c.			$N=0.1052$ $C=3.0$ c.c.		
t	x	k	t	x	k
89	6.5	58.2	59	11.7	124
156	11.7	61.4	109	21.0	124
223	16.2	60.5	155	28.8	123
280	20.2	61.0	205	36.0	120
408	28.3	60.5	266	45.4	120
496	33.3	60.7	377	56.5	123
1159	63.8	58.9	457	70.0	119
1409	72.9	59.1	632	86.7	116
1694	81.5	58.9	1253	127.5	116
1869	85.9	58.2	1713	145.7	121
2664	102.3	59.1	∞	166.4	...
2967	107.7	60.5	...	...	...
∞	129.0	...	...	...	...

$k_m=59.9$ $k'=60.6$ $k_m=121$ $k'=57.5$

Diethyl succinate, methyl alcohol

$N=0.0456$ $C=2.0$ c.c.			$N=0.4046$ $C=2.0$ c.c.		
t	x	k	t	x	k
46	7.4	204	23	6.9	421
108	15.5	192	44	12.7	421
136	19.0	192	86	22.5	414
210	27.7	195	157	36.1	419
256	32.4	194	278	51.5	416
316	37.7	193	379	60.1	426
403	64.6	193	∞	75.0	...
579	56.1	192	...	...	...
∞	82.6	...	...	...	...
...	...	...	...	...	...
...	...	...	...	...	...
...	...	...	...	...	...
...	...	...	...	...	...

$k_m=193$ $k'=212$ $k_m=419$ $k'=200$

Dimethyl adipate, ethyl alcohol

$N=0.0523$ $C=2.9$ c.c.			$N=0.1001$ $C=3.05$ c.c.		
t	x	k	t	x	k
61	8.8	131	68	15.2	219
110	14.9	126	110	23.8	222
175	22.8	127	157	32.4	222
271	32.8	124	208	40.9	224
350	40.2	123	274	50.4	224
506	53.1	123	389	64.2	225
640	63.1	125	471	72.2	227
1373	94.7	127	622	82.9	225
∞	114.7	...	∞	110.0	...
...	...	...	...	...	...

$k_m=125$ $k'=120$ $k_m=224$ $k'=112$

Diethyl adipate, methyl alcohol

$N=0.0532$ $C=3.0$ c.c.			$N=0.1122$ $C=3.0$ c.c.		
t	x	k	t	x	k
20	9.2	460	15	14.5	1060
43	19.0	465	25	22.8	1050
75	31.2	472	40	33.2	1025
97	38.1	465	79	54.7	1020
135	50.1	481	95	61.7	1030
188	61.6	472	121	70.3	1025
240	70.8	469	149	77.6	1000
317	81.2	469	186	84.6	1040
450	92.6	479	∞	98.8	...
∞	104.8	...	...	...	...

$k_m=470$ $k'=442$ $k_m=1030$ $k'=459$

Dimethyl suberate, ethyl alcohol

$N = 0.0578$ $C = 2.9$ c.c. $N = 0.1046$ $C = 2.9$ c.c.

t	x	k	t	x	k
51	5.5	142	73	14.4	237
102	10.7	143	120	22.6	237
182	17.6	139	172	30.4	237
247	22.6	137	214	36.2	237
347	29.8	137	271	42.7	235
407	33.2	135	325	48.5	235
561	43.5	144	376	53.1	235
1298	66.1	141	503	63.2	237
1458	68.9	142	683	73.0	239
∞	78.6	...	∞	90.8	...

$k_m = 140$ $k' = 121$ $k_m = 237$ $k' = 113$.

Dimethyl sebacate, ethyl alcohol

$N = 0.0523$ $C = 2.8$ c.c. $N = 0.1046$ $C = 3.0$ c.c.

t	x	k		x	k
60	4.5	127	84	12.1	232
116	8.3	126	127	17.7	237
227	15.2	125	184	75.2	250
403	24.4	126	253	31.9	250
1200	47.6	126	343	39.3	251
1561	53.0	129	480	46.6	239
∞	61.1	...	∞	68.1	...
...	...	..	...	...	...
...	...	...	...	...	...
...	...	...	...	...	...

$k_m = 126$ $k' = 121$ $k_m = 243$ $k' = 116$.

Diethyl tartrate, methyl alcohol

$N = 0.059$ $C = 2.323$g. $N = 0.1095$ $C = 2.24$g.

t	x	k	t	x	k
41	3.5	81.9	34	5.6	185
97	8.2	82.5	54	8.4	180
158	12.9	81.6	90	13.5	178
240	18.8	80.9	108	15.8	177
308	23.1	79.1	147	20.8	177
358	26.0	77.9	200	27.3	179
454	32.3	79.3	246	32.5	180
1311	68.8	79.1	517	55.9	185
1435	72.3	79.1	∞	90.7	...
1763	79.6	77.9	...	...	...
∞	106.5	...	...	...	...

$k_m = 80.0$ $k' = 76.5$ $k_m = 180$ $k' = 82.3$.

Diethyl malate, methyl alcohol

$N = 0.0423$ $C = 2.6$ c.c. $N = 0.106$ $C = 2.55$ c.c.

t	x	x calc.	t	x	x calc.
33	9.0	9.0	31	13.4	13.3
65	16.6	16.6	58	21.9	21.9
107	25.2	25.2	82	28.1	28.0
167	35.6	35.4	113	34.2	34.2
201	40.3	40.3	168	41.7	41.8
250	46.3	46.3	233	47.5	47.7
289	50.5	50.5	307	52.0	52.3
511	66.4	66.4	456	58.4	58.2
1234	84.6	86.5	668	64.0	63.4
∞	102.0	...	∞	74.6	...
...	...	...	...	...	...

$k_1 = 469$ $k'_1 = 554$ $k_1 = 1115$ $k'_1 = 545$

$k_2 = 98.5$ $k'_2 = 116$ $k_2 = 184$ $k'_2 = 87$

Examination of the figures in Table II reveals the fact that with dimethyl oxalate there is a slight tendency for the values of k to increase as the reaction proceeds, while in the case of diethyl oxalate the reverse is to be seen. This would imply that the OMe group in EtOOC.COOMe is replaced more readily than it is in MeOOC.COOMe, and that OEt in EtOOC. COOEt is replaced more readily than in EtOOC.COOMe; in other words, the methyl group causes a slight retardation. The experimental results are not sufficiently accurate to allow the two velocity coefficients to be calculated. A similar effect is not seen in the case of the esters of other symmetrical acids, doubtless owing to the wider separation of the reacting groups. In all these cases the reaction appears to be a unimolecular one within the limit of experimental error indicating that the velocity of replacement of both groups is the same.

With diethyl malate the results are of a different order. The value of k calculated according to formula (3) fell from 279 to 143 with the more dilute catalyst and from 635 to 292 with the more concentrated. On applying equation (4) with the values of K_1 and K_2 shown in the table, a very satisfactory agreement between observed and calculated values was found, indicating that the velocity coefficient for one group was about five times that for the other. The values for K_2 are not in very good agreement possibly owing to the fact that as the reaction approaches completion the simple equation no longer holds, and also because a small experimental error towards the end of the experiment has a large effect on the value of K_2.

The values of K (the velocity coefficient calculated for 0.05N acid) for all the esters with the single exception of diethyl adipate are smaller for the more concentrated catalyst, indicating that the more dilute acid is relatively more active, although the differences are slight and in many cases not greater than the experimental error.

The examples given show that the concentration of ester decreases in an exponential manner towards the equilibrium point as a limit. This is necessarily an approximation since the reaction is in reality more complex, particularly towards the end when the reverse reaction becomes appreciable. In most cases it is possible to calculate the equilibrium constant with sufficient accuracy and from this to deduce the true velocity coefficients. For example in the case of the esters of succinic acid k' is 60.6 for the methyl ester and 212 for the ethyl ester at catalyst concentrations very near to $0.05N$. Hence the equilibrium constant is approximately 212/60.6 or 3.50. The initial ratio of molecules of alcohol to ester is 46 :1 in the first reaction and 99 :1 in the second.

Hence if x and y are the molecular concentrations of original ester at equilibrium, the initial concentration being 1

$$x\,(45+x)/(1-x)^2=(1-y)^2/y\,(98+y)=3{\cdot}5$$

whence $x=0.067$ and $y=0.003$. In other words 6.7 per cent of ester remains unchanged at equilibrium in the first case, while in the second the conversion is over 99 per cent. The total volume change for the methyl ester would thus be 138 if the reaction went to completion and a more accurate value for k is obtained by using this figure instead of 126 and recalculating the values for the initial stages only. It may be shown that when v is small, $\ln(1-v/V)$ is inversely proportional to V so that if V increases by $100x$ per cent in formula (4), k diminishes in the same proportion in the initial stages. Since in most of the reactions studied k was constant within the limit of experimental error, a sufficient approximation to the correct value can be obtained by diminishing the mean k_m by $100x$ per cent and this has been done in the following table. The actual values of x varied from 0.051 to 0.072 for all the methyl esters except methyl azelate for which it was only 0.028 owing to the small quantity used. For the ethyl esters the value was in all cases 0.004 or less and no correction has been applied. For the three esters in which only one reaction was studied, the equilibrium constant was assumed to be 4.0

Table III.

Corrected velocity coefficients for 0.05 N acid

Acid		Methyl ester	Ethyl ester	Equilibrium constant	Esterification (Kailan)
Oxalic	...	248	762	3·25	414
Malonic	...	39·5	142	3.6	142
Succinic	...	56.3	212	3·75	207
Adipic	...	111	442	4.0	336
Suberic	...	113	...	...	...
Azelaic	...	114	...	...	...
Sebacic	...	114	...	...	...
Tartaric	...	...	76.5	...	68
Malic (a)	...	...	554	...	284
(b)	...	...	116	..	...

It will thus be seen that the velocity coefficients are greatest in the case of oxalic acid and least for malonic acid; as the number of carbon atoms increases the coefficients also increase until a constant value is reached. These results are analogous to those of Kailan (*loc. cit.*) for the velocity of esterification, which are also given in the table after multiplying by a factor to equalise the values for malonic acid. This author did not extend his measurements to the higher acids of the series. He states that the values for oxalic and malonic acids were not very reliable because decreasing results were obtained as the reaction proceeded, but the large difference between the coefficients for alcoholysis and esterification in the case of the former acid is somewhat remarkable and can scarcely be attributed to experimental error or the action of water.

Kolhatkar's figures for the monobasic acids show that methyl acetate reacts with ethyl alcohol nearly twice as rapidly as methyl oxalate under similar conditions ($k=430$). There is however, no minimum at the second member in this series, k for methyl propionate and butyrate being 245 and 137 respectively. The last figure approaches that for the higher dibasic acids (114) and it seems probable that if measurements were extended to long-chain monobasic acids, the figures for the two series would coincide. It appears therefore that the replacement of CH_3 in the monobasic acids by COOMe produces a large retardation for the second and third members and little or no effect when the number of carbon atoms is increased. These results bear a close resemblance to the effect of introducing an *iso*propyl group into the normal fatty acid molecule in the case of esterification as shown by Bhide and Sudborough (*J. Indian Inst. Sci.*, 1925, **8**, 91) their results being reproduced in Table IV together with those of Kolhatkar and some of the present series.

Table IV.

Alcoholysis		*Esterification*	
Ester	*k*	*Acid*	*k*
$CH_3.COOMe$ …	430	$CH_3.COOH$ …	796
$MeOOC.COOMe$ …	248	$(CH_3)_2CH.COOH$ …	156
$CH_3.CH_2.COOMe$	245	$CH_3.CH_2.COOH$ …	550
$MeOOC.CH_2.COOMe$ …	40	$(CH_3)_2CH.CH_2COOH$ …	52
$CH_3(CH_2)_2.COOMe$ …	137	$CH_3(CH_2)_2.COOH$ …	270
$MeOOC.(CH_2)_2.COOMe$	56	$(CH_3)_2CH.(CH_2)_2.COOH$	247
$CH_3.(CH_2)_4.COOMe$ …	?	$CH_3.(CH_2)_3.COOH$ …	268
$MeOOC.(CH_2)_4.COOMe$	111	$(CH_3)_2.CH.(CH_2)_3.COOH$	267

In both cases the maximum retardation occurs when the replacement is made on the carbon atom in the β-position.

The above authors have also measured the esterification velocity coefficients for adipic, pimelic and suberic acids and have recorded a slight decrease, the values in arbitrary units being 307, 282 and 264 respectively. These results appear somewhat abnormal.

Kailan did not calculate the two velocity coefficients for malic acid, but his figures approximate to those obtained for alcoholysis. The substitution of one atom of hydrogen in succinic acid by OH thus accelerates the velocity of reaction of one COOH or COOMe-group and retards that of the other. Kailan concluded from his results with mandelic and phenylacetic acids (*Sitzungsber. Akad. Wiss. Wien,* 1907, **116**, IIb, 1094) that an OH group in the α-position slightly retards the rate of reaction and consequently that the COOH-group next to the CHOH-group in malic acid esterifies less rapidly. Drushel (*Amer. J. Sc.,* 1915, IV, **39**, 113), however, from a study of the hydroxypropionic esters has shown that in the case of hydrolysis, the substitution of an OH-group in the α-position accelerates the reaction and has a marked retarding effect in the β-position, the coefficients for ethyl propionate and α-and β-hydroxypropionic esters being 71.2, 76.1 and 16.3 respectively.

Retardation by a β-substituent is in accordance with the results given in Table IV and it seems probable that Kailan's assumption is incorrect and that the COOH-group adjacent to the CH_2-group in malic acid is the less reactive. This retarding effect would also explain to some extent the very low value for tartaric acid.

The equilibrium constants of the dibasic esters increase from 3.25 to 4.0 for the members of the series from oxalic to adipic acid, a variation somewhat greater than that found by Kolhatkar for the ethyl and methyl esters of acetic, propionic and *n*-butyric acid for which the values were 3.5, 3.8 and 3.7 respectively.

We wish to take this opportunity of expressing our thanks to Mr. S. K. Kulkarni Jatkar for much assistance during the course of our experiments.

SUMMARY

1. The velocity of alcoholysis of methyl and ethyl esters of oxalic, malonic, succinic, adipic, suberic, azelaic, sebacic, tartaric and malic acids with ethyl and methyl alcohol in presence of hydrochloric acid as a catalyst has been studied at 30° by a dilatometric method.

2. In the case of the symmetrical acids the reaction proceeds according to the rule for a unimolecular reaction, indicating that the replacement of OMe by OEt at one end of the molecule does not appreciably affect the rate of reaction of the other COOMe-group. Oxalic acid is an exception but the departure from the rule is so small that the two velocity coefficients cannot be calculated with accuracy.

3. The two ester groups in malic acid react at different rates, the one adjacent to the CH_2-group being apparently the less reactive. The velocity observed agrees with that calculated on the hypothesis that two unimolecular reactions take place simultaneously at different rates.

4. In the series of unsubstituted acids, oxalic acid has the largest velocity coefficient and malonic acid the smallest. The values for adipic acid and the succeeding members are all equal.

5. The reaction velocity is very nearly proportional to the concentration of catalyst in the range studied.

6. The equilibrium constant increases slightly from oxalic to adipic acid.

7. Alcoholysis of these acids bears a considerable resemblance to the esterification as measured by Kailan.

Department of General Chemistry,
Indian Institute of Science,
Bangalore.

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