120. *Acid-catalysed Alcoholysis. Part I.*

By M. F. CARROLL.

A method for studying acid-catalysed alcoholysis is described. In non-polar solvents the reaction velocity is proportional to the ester and catalyst concentration and is substantially independent of the alcohol concentration within the limits of the work reported. As in acid-catalysed esterification, secondary alcohols react much less readily than primary alcohols, and the difference in reactivity is very much greater than in the alcoholysis of esters of acetoacetic acid.

The addition of secondary alcohols to an ester–primary alcohol–catalyst system causes a marked lowering of the rate of reaction and an explanation is offered to account for this.

THE author (XIth International Congress of Pure and Applied Chemistry) has recently shown that the alcoholysis of esters containing an active methylene group can be studied by a simple method involving the removal of the alcohol formed by azeotropic distillation. It was found that this reaction was not markedly affected by catalysts, and the rate of reaction was proportional to the ester concentration and independent of the alcohol concentration. In order to compare the reaction velocity with that of the acid-catalysed alcoholysis of simple esters, the same procedure was used with some aliphatic esters. The rate of reaction was found to be proportional to the ester and catalyst concentration and independent of the alcohol concentration, over a wide range.

Goldschmidt *et al.* (*Z. physikal. Chem.*, 1907, **60**, 728; 1929, **143**, 139, 278) have shown that in acid-catalysed esterification, the reaction velocity is given fairly accurately by the expression :

$$d[R\cdot CO_2R']/dt = k[R\cdot CO_2H][R'\cdot OH_2^+] \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which for a constant catalyst concentration reduces to the usual first-order equation for k. Smith (*J. Amer. Chem. Soc.*, 1939, **61**, 254), working with methanol and various organic acids and hydrochloric acid as catalyst, showed that a correction should be applied on account of the oxonium ion produced in the esterification. The value of k thus obtained remained constant up to about 50% conversion, but a downward drift was then obtained. Leyes and Othmer (*Ind. Eng. Chem.*, 1945, **37**, 968) investigated the esterification of acetic acid and butanol with sulphuric acid as catalyst, but their work was complicated by the polyfunctional behaviour of the catalyst, although, in principle it confirms the findings of Goldschmidt and Smith.

Thus previous work in this field was affected by three disturbing factors : (1) the organic acid is a catalyst for the reaction, (2) water produced in the esterification produces a different species of catalyst, *i.e.*, the ion H_3O^+ replaces the ion $R\cdot OH_2^+$ as the reaction proceeds, and (3) the actual catalyst itself may change and in some cases the rate of decay of the catalyst may seriously affect the results. In the present work these effects have been avoided, for with alcoholysis (1) and (2) no longer apply and the ions $R''\cdot OH_2^+$ and $R'\cdot OH_2^+$ are almost identical :

$$R\cdot CO_2R' + R''\cdot OH_2^+ \rightleftharpoons R\cdot CO_2R'' + R'\cdot OH_2^+ \quad . \quad . \quad . \quad . \quad . \quad (2)$$

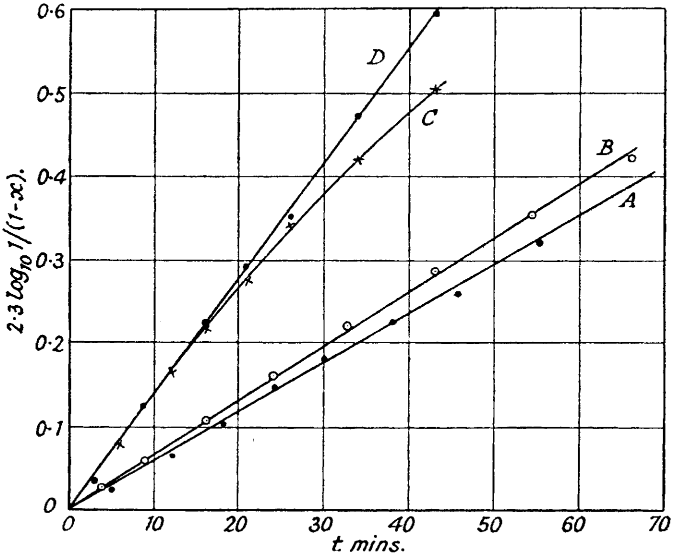
Moreover, in the present paper the system becomes irreversible, the alcohol $R'\cdot OH$ being removed as fast as it is formed. The method has been described in detail (*loc. cit.*) but the essential features are as follows : A high-boiling ester $R\cdot CO_2R'$, a high-boiling alcohol $R''\cdot OH$, and a stable catalyst react in a solvent at the boiling point of the mixture, the low-boiling alcohol

R′·OH being removed rapidly by the boiling solvent vapour. The alcohol content of the distillate is measured by refractive-index determinations. The concentration is maintained, and the temperature controlled, by the addition of pure solvent to replace that which has distilled.

The choice of the catalyst presents some difficulty; hydrochloric acid is volatile, and apart from the above-mentioned disadvantage, sulphuric acid tends to be reduced at higher temperatures, and shows a high rate of decay during the progress of the reaction. Sulphonic acids were found to be satisfactory under the conditions of the experiments, and *m*-xylenesulphonic acid, which is easily obtained in a pure crystalline form as the dihydrate, was used throughout this work. The rate of decay was found to be small enough to be ignored in most cases, but at high temperatures a slight correction is necessary.

The method is somewhat restricted, as the temperature is mainly determined by the raising of the boiling point of the solvent by the dissolved reagents, and for this reason most of the measurements were made with equimolecular proportions, which fixed the b. p. of the solution at 118° and permitted a comparison to be made at this temperature. Also, by varying suitably the ratio of alcohol to ester, it was possible, within certain limits, to obtain the same elevation of the b. p. of the solvent and consequently to compare reaction rates at different concentrations at the same temperature.

Fig. 1.



The equation of the unimolecular reaction was found to represent the results accurately up to a conversion of 60—70%, and this is shown in Fig. 1, curves *A* and *B* referring to ethyl laurate and methyl phenylacetate respectively with octan-1-ol in toluene (see Table I). Curve *C* shows a similar result with ethylbenzene as solvent, and *D* shows this result corrected for rate of decay of the catalyst.

The effect of catalyst concentration (*c*) on the rate of reaction is shown in Table I, which indicates that the reaction velocity is approximately proportional to the catalyst concentration, although there is a small but probably significant dilution effect.

Table I.

Ethyl laurate and octan-1-ol, 1 mol./l. in toluene at 118°.

c, mols./l.	0·03	0·015	0·0075
$k \times 10^3$	13·3	6·45	3·23
k/c	0·443	0·431	0·431

Ethyl phenylacetate and octan-1-ol, 1 mol./l. in ethylbenzene at 145°.

c, mols./l.	0·01	0·0068	0·005
$k \times 10^2$	2·64	1·58	1·15
k/c	2·64	2·38	2·30

Tables II and III give the values of *k* for several esters and alcohols. Varying the proportions of alcohol and ester has little effect on the rate of reaction calculated on the ester concentration.

TABLE II.

Ester and octan-1-ol at 1 mol./l.; catalyst = 0·015 mol./l. in toluene at 118°.

	10^3k.		10^3k.		10^3k.
Ethyl laurate	6·45	Ethyl phenylacetate	12·1	Ethyl benzoate	1·06
Ethyl heptoate	5·7	Methyl phenylacetate	14·9		

(The value of *k* at this temperature was not measurable for ethyl salicylate on account of the low rate of reaction.)

Ester and octan-1-ol at 1 mol./l.; catalyst = 0·01 mol./l. in ethylbenzene at 145°.

	10^2k.		10^2k.		10^2k.
Methyl phenylacetate	3·18	Ethyl phenylacetate	2·64	Butyl phenylacetate	1·10

TABLE III.

Alcohol and ethyl phenylacetate at 1 mol./l. in toluene at 118°; catalyst = 0·015 mol./l.

	10^3k.		10^3k.		10^3k.
Octan-1-ol	12·1	Benzyl alcohol	8·3	Menthol	0·6
2-Ethylhexanol	9·0	Octan-2-ol	0·8	Phenylmethylcarbinol	0·7

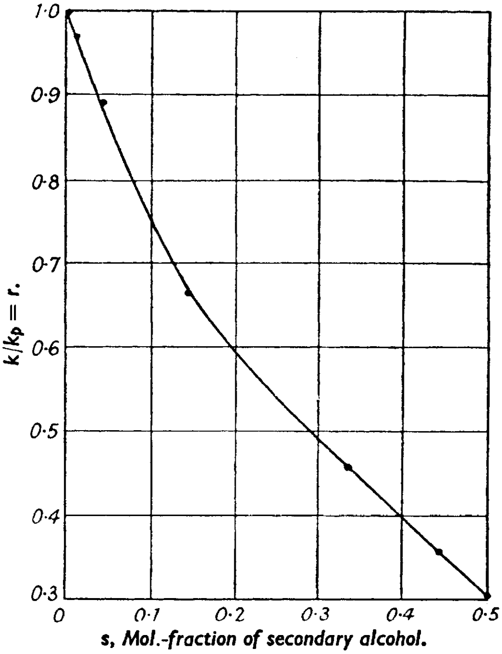
This is shown in Table IV, where the probable error is about 0·05 for equimolecular proportions but increases to 0·10 for the higher ratios. Catalyst and ester concentration are maintained constant. It is seen that the excess of alcohol does not increase the rate of reaction as would be expected from the simple bimolecular mechanism.

TABLE IV.

Ethyl phenylacetate and octan-1-ol in toluene at 118°; catalyst = 0·015 mol./l.

Ratio of ester to alcohol	1 : 1	1 : 2	2 : 1	1·5 : 1
10^3k	12·1	11·3	10·5	11·0

FIG. 2.



The effect of adding various quantities of a less reactive alcohol to a system containing equimolecular quantities of an ester and a primary alcohol is shown in Fig. 2. A very marked decrease in the value of *k* is observed.

Goldschmidt and Smith had assumed that in acid esterification the catalyst reacted as the ion $R{\cdot}OH_2^+$, and this view is supported by the results above, although the range investigated is somewhat limited. This implies that esterification can be treated as a special case of alcoholysis and that the mechanism of both is substantially the same.

The concentration of the active ion $R{\cdot}OH_2^+$ is given by the expression

$$R{\cdot}OH + HX \rightleftharpoons R{\cdot}OH_2^+ + X^- \quad (3)$$

and the extent of the protolysis may be expected to be less than in more polar solvents, but it appears to be great enough to make the catalytic effect proportional to the catalyst concentration over a wide range, as is shown by the results in Table I.

The very much lower reaction rate with secondary alcohols is probably due to the greater energy of activation and to variation of the *P* factor, as the extent of the ionisation due to reaction (3) should not be greatly different from that of primary alcohols, the dielectric constants of these alcohols being of the same order. Smyth and Stoops (*J. Amer. Chem. Soc.*, 1929, **51**, 3330) found for octan-1-ol, ε = 7·2 at 58°, and for octan-2-ol, ε = 5·6 at 56°. This view is supported by the constancy of k/c for secondary alcohols. Thus with octan-2-ol at catalyst concentration $c = 0{\cdot}015$ mol./l., $k = 0{\cdot}8 \times 10^{-3}$ and $k/c = 0{\cdot}053$, and with $c = 0{\cdot}075$ mol./l., $k = 4{\cdot}2 \times 10^{-3}$ and $k/c = 0{\cdot}056$.

That the decrease in the value of k shown in Fig. 2 is not due to the dielectric effect can be inferred from the results in Table IV, where increase in the alcohol concentration which would increase the value of ε has no significant effect on the reaction velocity. It may be assumed, therefore, that the decrease in k is caused by the sharing of the available H^+ ion. Thus for added polar compounds which do not react with the ester

$$R_p{\cdot}OH + BH^+ \rightleftharpoons R_p{\cdot}OH_2^+ + B \quad . \; . \; . \; . \; . \; . \; . \quad (4)$$

If p, b, c, and α are the concentrations of the primary alcohol, the polar compound B, the catalyst, and the primary alcoholonium ion respectively, then

$$K = \frac{R_p{\cdot}OH_2^+][B]}{[R_p{\cdot}OH][BH^+]} = \frac{\alpha[b - (c - \alpha)]}{(p - \alpha)(c - \alpha)} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (5)$$

Complete ionisation being assumed, the reaction rate is proportional to the catalyst concentration c, and for the mixture $\alpha = ck_m/k_p$, where k_p and k_m are the rate constants for the primary alcohol alone and the mixture respectively.

When the added polar compound, *e.g.*, a secondary alcohol, takes part in the reaction

$$k_mc = k_p[R_p{\cdot}OH_2^+] + k_s[R_s{\cdot}OH_2^+] = k_p\alpha + k_s(c - \alpha) \quad . \; . \; . \; . \quad (6)$$

where the suffix s refers to the secondary alcohol. If the primary and secondary alcohol ions react independently in proportion to their separate reaction rates, and putting $k_p/k_s = n$, we have

$$k_mc = k_p[\alpha + (c - \alpha)/n]$$

and

$$\alpha = c(rn - 1)/(n - 1) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (7)$$

where $r = k_m/k_p$.

Substituting the calculated value of α, using $n = 12{\cdot}1/0{\cdot}8$ (see Table III) in equation (5), it is found that $K = 0{\cdot}35$ for octan-1-ol and octan-2-ol. For octan-1-ol and *m*-cresol $K = 2{\cdot}13$, the relative affinity for the proton being in the order of the strengths as base of the compounds used.

The assumption of complete ionisation in equation (6) is open to objection, but it is reasonable to assume an effective hydrogen-ion concentration of the same order where the dielectric constant is nearly equal. If an effective concentration of catalyst is postulated such that $c' = c - HX$ in each case, and arbitrary values of c' are used in place of c in equation (6), it will be found that where c'/c is between 0·5 and 1, the constancy and mean value of K are not appreciably affected. It may also be expected that some of the available H^+ ion is bound to the ester, but since the total ester species remains the same and is sensibly constant, the above argument applies equally well.

EXPERIMENTAL.

Materials.—The toluene used as solvent was obtained by the pyrolysis of dibenzyl ether, which gives a chemically pure product. The ethylbenzene was made from ethylene and pure benzene. Fractions of constant refractive index were selected from large-scale distillation. In each case redistillation gave fractions with a variation of only 0·0002 in the refractive index.

The esters and alcohols used were selected from readily available raw materials, the starting point in each case being a chemically pure product, which was further fractionally distilled and middle fractions selected. The catalyst was made by sulphonating pure *m*-xylene, adding sufficient water to obtain the *m*-xylenesulphonic acid as the dihydrate, and crystallising to constant acidity.

The apparatus has been previously described.

Method.—This differs in the order of addition of the reagents. The alcohol and catalyst and a known amount of solvent were heated to boiling in the flask, water being removed by the solvent and the volume of solution being maintained constant. The distillation was continued until no more water distilled and the solvent had a constant refractive index. At this point, while the solvent was still boiling, the ester was added, vigorous heating being continued to maintain the distillation. The zero point was taken when all the ester had been added and the thermometer at the top of the column was within 1° of the b. p. of the solvent. Fractions were collected at intervals, dry solvent replacing that distilled to maintain the volume constant. The temperature remained fairly constant within ±0·2° but tended to fall towards the end of the experiment, but this could be overcome by increasing the flooding of the column, and hence the back pressure, by removing the shield. Practically all the results were obtained with $\frac{1}{3}$ mol. of alcohol and ester in $\frac{1}{3}$ l. of solution, but where the ratios were varied the b. p. elevation was not the same and it was necessary to adjust this to the standard temperature by varying the pressure in the system by changing the column packing. Although this is successful, if somewhat troublesome, yet it seriously limits the concentrations that can be used.

Table V gives the results for ethyl laurate and octan-1-ol at 1 mol./l. concentration in toluene, and shows the method of calculation, k being the unimolecular constant : $k = (2{\cdot}3/t) \log 1\ (1 - x)$.

TABLE V.

Alcohol and ester = ⅓ mol., catalyst 0·55 g. (= 0·0025 mol.) in ⅓ l. of solution ($n_D^{20°}$ of toluene = 1·4947, uncorr.).

Time, mins.	Temp. of solution.	Temp. of vapour.	Distillate, g.	$n_D^{20°}$.	Alcohol, % (x), in distillate.	10^3k.
Alcohol and catalyst in :						
—	112°	110°	—	1·4940		
—	115	110	—	1·4940		
—	116	110	—	1·4946		
Ester added :						
0	118·3	110	18·15	1·4925	(0·31 g. = 0·007 mol.)	
7	118·2	109	8·25	1·4876	2·89	4·21
14	118·1	110	10·8	1·4867	7·29	5·41
21	118·0	110	10·85	1·4870	12·53	6·37
30	118·3	110·5	19·4	1·4889	18·06	6·64
41	118·0	110·5	10·8	1·4850	23·11	6·40
52	118·0	110	18·1	1·4884	28·47	6·45
63	118·0	110·5	20·7	1·4895	33·43	6·46
75	118·0	110·5	16·4	1·4882	38·44	6·47
91	118·2	110·5	24·6	1·4900	43·70	6·31

Rate of decay of catalyst. A much larger quantity of catalyst was used in a control experiment in order to be able to estimate more accurately the rate of disappearance. 55·5 G. of catalyst and 65 g. of octan-1-ol were heated in 500 ml. of toluene to 118° while water was removed azeotropically. After removal of water, a sample on titration with bromophenol-blue as indicator gave normality = 0·49 (theory = 0·50). Further,

after 3 hours, normality = 0·474, loss per hour = 1·1%
after 15 hours, normality = 0·394, loss per hour = 1·27%.

Reference to Table I shows that this rate of decay is insignificant in respect to the total time.

The same quantities of reagents were used with ethylbenzene as solvent at 145°. After 3½ hours 50% loss was observed, or approximately 14% per hour. This high rate of decay has been allowed for in Fig. 1 by applying the correction, $x_{\text{corr.}} = x_{\text{obs.}}\ (1 + at)$, where a is the rate of decay per minute.

Variation of alcohol to ester ratio. The b. p. elevation due to the ester is about twice that due to the alcohol; consequently, some variation in procedure is necessary where the alcohol : ester ratio is varied. When using a deficiency of ester it is only necessary to use more packing in the column to obtain the required b. p., *i.e.*, 118°. With quantities greater than 1 mol. of alcohol and ester, the minimum packing was used and a slight vacuum was applied to aid removal of the distillate and maintain the temperature at 118°. This manipulation is somewhat difficult and in consequence the error is somewhat greater.

The results for the addition of the secondary alcohol to the alcoholysis system were obtained as follows. The ester, catalyst, and primary alcohol were maintained at constant concentration, and secondary alcohol added. With larger amounts of secondary alcohol it was necessary to counteract the elevation of the b. p. by the procedure given above.

In the following table s is the fraction of secondary alcohol of the total alcohols, r is the ratio of the reaction velocity constant without addition to that obtained by adding the fraction s of secondary alcohol.

s	0	0·01	0·047	0·143	0·25	0·333	0·444	0·5
10^3k	12·1	11·7	10·8	8·1	6·7	5·6	4·3	3·6
r	—	0·97	0·89	0·665	0·55	0·46	0·36	0·30
a	0·015	0·0146	0·0132	0·010	0·0078	0·0063	0·0047	0·00375
K	—	0·365	0·354	0·326	0·365	0·355	0·360	0·330

Mean $K = 0{\cdot}35$.

Similarly for *m*-cresol, when $s = 0{\cdot}50$, $k = 8{\cdot}2 \times 10^{-3}$, $r = 0{\cdot}68$, $a = cr = 0{\cdot}0702$, and $K = 2{\cdot}13$.

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