468. *Acid-catalysed Alcoholysis. Part II. Aprotic Solvents.*

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Methods for the direct measurement of the reaction velocity of acid-catalysed alcoholysis have been devised, permitting a study of the effect of varying the concentration of the reagents. When octan-1-ol and ethyl acetate in toluene are used at 1 mole per l., the reaction velocity is approximately proportional to the ester and catalyst concentration. It is almost independent of the alcohol concentration over a wide range, but at low alcohol concentrations marked variations are observed. The rate constant increases markedly with decreasing ester concentration.

These findings have been explained on the basis of an extension of the hypothesis advanced in Part I, and it is now suggested that the sharing of the catalyst H^+ ion between the alcohol and the ester gives rise to the above effects. At equimolecular concentrations the distribution of H^+ ion between alcohol and ester is in the approximate ratio 3 : 2.

The method used in Part I of this work to study acid-catalysed alcoholysis was not sufficiently flexible to permit of accurately comparing the variation of reaction rate with concentration, and the present work describes an attempt to apply more conventional methods. The aim of this investigation and the reasons for preferring the alcoholysis reaction have been described in Part I.

In this reaction, with a suitable choice of reagents, the activities of the ions can be almost identical and the solutions remain homogeneous. The reaction rate can be measured if one of the esters in the system can be removed and the other determined by the ester-value method. For this purpose two procedures were employed. In the first, a low-boiling ester, a high-boiling alcohol, and the catalyst were maintained at a constant temperature in a suitable solvent. After a known interval the solution was transferred to an evaporating vessel and vacuum applied rapidly, the reaction being stopped by the temperature lowering and the removal of the low-boiling ester. The residual high-boiling ester formed was then determined directly by an ester value, allowance being made for the catalyst. The method is fairly general, but the time error is not easily assessed; hence a second method was used as a check. In this method the reaction was stopped by pouring the solution on to a standard sodium hydrogen carbonate solution to remove the catalyst and evaporating the solvent and low-boiling ester as before. Several control tests were necessary for both methods. In addition the uncatalysed reaction was found to be negligible under the conditions of the experiments.

The reagents used were ethyl acetate as low-boiling ester, octan-1-ol as high-boiling alcohol, *m*-xylenesulphonic acid as catalyst, and toluene as solvent.

The method used in Part I had the advantage that the reaction was, in effect, irreversible, whereas in the present work allowance must be made for the reversible reaction. If first-order kinetics are used, the equation for the rate of reaction for any given catalyst concentration is:

$$-\mathrm{d}x/\mathrm{d}t = k_1(a - x) - k_2x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where a is the initial concentration of the low-boiling ester and x the concentration of the high-boiling ester at time t. For the reagents used, the equilibrium constant $K \simeq 1$ and $k_1 \simeq k_2$, and for convenience of calculation the expression

$$k = (2{\cdot}3/2t) \log_{10} a/(a - 2x) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

gives a good approximation for small values of x.

The variation of k with time is shown in Table I, which gives the values for the ester and alcohol at molar concentrations in toluene at 25°. The example therein, which is typical of several experiments at different concentrations, shows that k decreases slightly, but not so markedly as in Goldschmidt's study of acid-catalysed esterification (*Z. physikal. Chem.*, 1929, **143**, 139, 278).

TABLE I.

Time, mins.	61	125	227	368
x	0·035	0·068	0·116	0·170
$k \times 10^4$	5·93	5·85	5·81	5·64

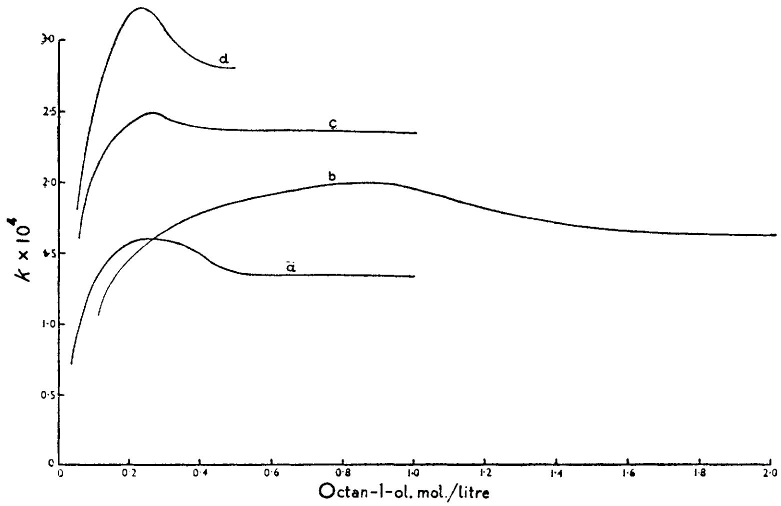
The relative constancy of k as the reaction proceeds has an important bearing on the subsequent work, as it was possible to make only one or two measurements of k at each concentration, and it was assumed that the value of k was independent of the concentrations. This is true for small values of x and in consequence the time intervals were chosen so as to make x as small as possible consistently with a low experimental error.

The effect of varying the ester, alcohol, and catalyst concentration separately was therefore investigated by determining a value of k at varying concentrations of each. Table II shows the values of k for different catalyst concentrations in toluene at 25°. All concentrations are in moles per litre.

TABLE II.

Ester.	Alcohol.	Catalyst.	$k \times 10^4$.	$k/c \times 10^2$.
0·5	0·5	0·0083	1·10	1·32
0·5	0·5	0·010	1·33	1·33
0·5	0·5	0·019	2·38	1·25
0·5	0·5	0·050	5·97	1·20
0·5	0·5	0·100	11·40	1·14
1·0	1·0	0·0167	2·01	1·21
1·0	1·0	0·05	6·15	1·23
1·0	2·0	0·05	5·50	1·10

FIG. 1.



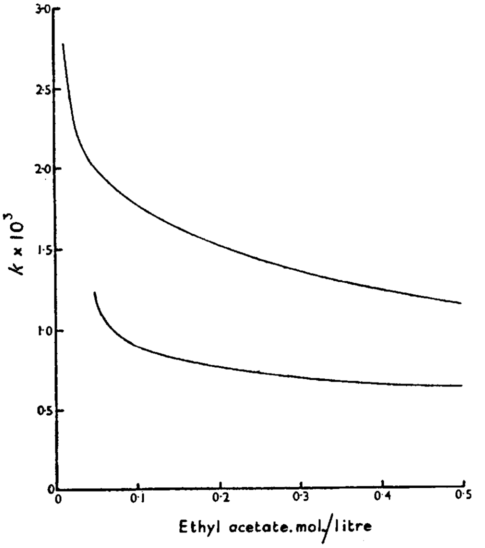
As will be seen from the table there is a small but significant decrease in the value of k/c with increasing catalyst concentration.

Fig. 1, curves a, b, and c, shows the effect of varying the alcohol concentration in toluene at 25°. Curves a and c are for the first and second methods, respectively, with an ester concentration of 0·5 mole per litre, and b is for the first method with an ester concentration of 1 mole per litre. In all cases k increases slightly as the alcohol concentration decreases, reaches a maximum—which varies with the ester concentration—and then falls rapidly.

In Fig. 2 is plotted the value of k against ester concentration with octanol concentration constant at 0·5 mole per litre.

In Part I it was shown that the addition of a polar compound to the reagents in a non-polar solvent reduced the reaction velocity considerably and this was explained by assuming that the catalytic H$^+$ ion was shared between the reacting alcohol and the added compound. It was also assumed that the ester and solvent took no part in the H$^+$ ion distribution and that ionisation was substantially complete. Neither assumption is justifiable except in a qualitative sense, but the experimental conditions did not permit of an accurate determination of the effect of varying the concentrations of the reagents. If, however, an added polar substance shares the H$^+$ ion, the ester reagent must be expected to do so. This view can be shown to be consistent with the results shown in Fig. 2 since, with the decrease in ester concentration, more of the H$^+$ ion is available for catalysing the alcoholysis.

FIG. 2.



At the beginning of the reaction the catalyst is shared according to the scheme:

$$\mathrm{ROH} + \mathrm{HX} \rightleftharpoons \mathrm{ROH_2^+} + \mathrm{X^-} \quad . \quad (3)$$

$$\mathrm{E} + \mathrm{HX} \rightleftharpoons \mathrm{EH^+} + \mathrm{X^-} \quad . \quad . \quad (4)$$

where ROH, E, and HX refer to the alcohol, ester, and catalyst, respectively. Since measurements were confined to initial changes only, the reverse alcoholysis reaction resulting in the production of the alcohol R′OH and ester E′ need not be considered as the total ester + alcohol concentration remains constant and there is no change in the distribution of H$^+$ ion. If p, e, and c are the initial concentrations of alcohol, ester, and catalyst, and α and β are the concentrations of alkyl oxonium ion and ester ion at equilibrium, then

$$K_1 = \frac{\alpha(\alpha + \beta)}{(p - \alpha)(c - \alpha - \beta)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$K_2 = \frac{\beta(\alpha + \beta)}{(e - \beta)(c - \alpha - \beta)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

These equations are too intractable for the evaluation of α, although in principle this is possible. To facilitate calculations it may be assumed, as in Part I, that ionisation of the catalyst is sufficiently complete to ignore the unionised-catalyst concentration. This is probable when p is large, as in the experiments on the variation of ester concentration. The equation therefore becomes:

$$\mathrm{ROH} + \mathrm{EH^+} \rightleftharpoons \mathrm{ROH_2^+} + \mathrm{E} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

and putting EH$^+$ $= c - \alpha$ and E $= e - (c - \alpha)$

$$K = \frac{\alpha[e - (c - \alpha)]}{(p - \alpha)(c - \alpha)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Also, the reaction velocity is:

$$V = k_0[\mathrm{Ester}]\alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and for any series of experiments $k/k_0 = \alpha$, where k is the observed velocity constant as defined by equation (2).

Various values were assigned to K, and α was then calculated from the quadratic equation derived from (8). Substituting these values and the results for k, the constancy of k_0 could be tested. The best value found for K is 1·5, and the calculated values for k_0 are given in Table III.

TABLE III.

Octan-1-ol, 0·5 mole/l. in toluene at 25°.

(*a*) Catalyst = 0·05 mole/l.

Ester, mole/l.	0·5	0·3	0·2	0·1	0·05
$k \times 10^4$	6·32	6·97	7·72	8·8	12·4
$a \times 10^2$	3·2	3·5	3·9	4·4	4·9
$k_0 \times 10^2$	1·98	1·99	1·98	2·0	2·52

(*b*) Catalyst = 0·10 mole/l.

Ester, mole/l.	0·5	0·2	0·1	0·06	0·04	0·03	0·02
$k \times 10^4$	11·4	15·2	18·4	19·5	20·5	21·7	27·4
$a \times 10^2$	6·0	7·8	8·8	9·3	9·5	9·6	9·7
$k_0 \times 10^2$	1·90	1·96	2·09	2·10	2·15	2·26	2·83

The value of k_0 remains constant over a wide range, but there is a marked tendency for it to increase at low values of e. Too much significance should not be attached to this increase because at this low concentration of ester the experimental error is relatively large; thus at $e = 0{\cdot}02$, the total ester corresponds to 4 c.c. of N-sodium hydroxide solution, and the ester formed (*i.e.*, x) is equivalent to 0·8 c.c. after deduction of the relatively large blank (0·4 c.c.). Thus an error of 0·2 c.c. would affect the results at low concentrations seriously, while having little effect at high concentrations. A factor tending to influence the results is the ionisation effect of equation (5) which would make the value of k_0 higher than that calculated from equation (8).

The dielectric effect has been considered in Part I, and in the present work the solvent has been considered only as a diluent which enables the concentrations to be varied. If the substrate is considered as a whole, the dielectric constant increases as the concentration of polar compounds increases, which would give a high value for k on account of the increased ionisation of reaction (3). The effect of the variation of the dielectric constant of the medium on the rate-determining step of the alcoholysis

$$\mathrm{ROH_2^+ + E \rightleftharpoons R'OH_2^+ + E'} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

is not so easily decided. It has been sometimes assumed that the variation of the reaction rate of esterification or hydrolysis in polar solvents is entirely a function of the dielectric effect.

In this work the total dielectric effect must be small, since an increase in the concentration of the relatively strongly polar octanol ($\varepsilon = 12{\cdot}6$ at 25°) has a smaller effect than the less polar ethyl acetate ($\varepsilon = 6{\cdot}03$; Krchma and Williams, *J. Amer. Chem. Soc.*, 1927, **49**, 2412). This has also been shown in Part I for the isomeric octanols; addition of the less polar secondary alcohol produces a greater decrease in the reaction rate than a corresponding amount of the primary alcohol.

The scheme proposed in equations (5) and (8) fails to account for the maxima in the curves of Fig. 1 and the fall in the reaction rate with increasing alcohol concentrations. However, at high alcohol concentrations, ion association becomes an important factor, and it follows that k_0 is really greater than the mean value of Table III and that the reaction rate should be measured at a greater dilution, but the advantage gained is offset by the greater experimental error involved in working at such low concentrations. The value of K obtained with the highest reliable value of k still remains within the range of $1{\cdot}5 \pm 0{\cdot}2$.

EXPERIMENTAL.

Materials.—Good-quality ethyl acetate was further purified by fractional distillation, and only the middle fractions of constant refractive index were used. The other materials were purified as described in Part I.

Apparatus.—The reaction tubes were of resistance glass 40 cm. long and 3 cm. in diameter. The vacuum-evaporator consisted of a two-necked flask with ground glass joints. One neck carried a short column packed with glass rings and connected to a high-vacuum system (1·0 mm. of Hg) of high capacity. A capillary tube was inserted in the other neck to ensure regular ebullition. The hydrolysis flask was of resistance glass with a ground glass joint connected to a condenser. All the apparatus was leached with acid and water until a control test showed no effect on the ester value.

Method 1.—Pure *m*-xylenesulphonic acid dihydrate was dissolved in some of the octanol, the solvent added, and water removed by distilling off the solvent–water azeotrope until the distillate was dry. The solution was then made up to the required strength by adding dry toluene. When it was necessary to vary the octanol concentration, only sufficient octanol was used to ensure solution of the catalyst and the requisite alcohol concentration was obtained by adding a 2N-solution of the octanol. A 2N-solution of ethyl acetate was prepared and the strength checked by the ester value. All solutions were made up at 25° and transferred at that temperature. Suitable quantities of reagents were pipetted into the reaction tube, zero time being taken as the end of the addition when the tubes were shaken to mix the contents. The period of addition was about 30 seconds, and the time error due to mixing was usually less than 1%. After a suitable time, the contents of the tube were poured into the evaporating vessel and the full vacuum applied, the temperature falling rapidly to −10°. When all the solvent had been removed, the residue was washed into the hydrolysis flask with pure ethanol and made up to 50 c.c. An excess of aqueous N-sodium hydroxide was added and the solution heated under gentle reflux for 2 hours. After the solution had been cooled, 100 c.c. of CO_2-free water were added and the whole titrated with standard acid. For small values of x weaker standard solutions were used, *e.g.*, 0·2 N. When the corrections found in the control tests are applied, the value of x is obtained directly from the titration difference. The following control tests were carried out. (i) Ester value on individual reagents—the titre was negligible. (ii) The strength of catalyst solution was determined by titration with standard alkali to bromophenol-blue. (iii) An ester value on the catalyst–octanol solution gave a titre varying with the catalyst concentration and ranged from 0·05 to 0·4 c.c. with N-sodium hydroxide. (iv) The reaction tube was rinsed with water after use, and the solution titrated. This was necessary to ensure that no catalyst had deposited during the reaction. (v) The correction actually applied was the overall result obtained by carrying out the process at zero time, *i.e.*, by applying the vacuum immediately on mixing. The titre obtained which included that due to the catalyst was used as the actual control.

Method 2.—The procedure is the same as in Method 1 except that the reaction is stopped by shaking with standard sodium hydrogen carbonate solution, separating the solvent layer, and removing the solvent and low-boiling ester under vacuum as before. By titrating the aqueous layer with standard acid it is possible to check the amount of catalyst used in each experiment. A correction must be applied to allow for the slight hydrolysis of the ester due to the aqueous hydrogen carbonate solution. This was determined by using known amounts of octyl acetate and noting the amount hydrolysed in the above procedure.

A typical examples of the results obtained by method 2 is given below in Table IV.

TABLE IV.

Ethyl acetate, 0·1 mole; catalyst, 0·004 mole; and octan-1-ol, made up to 200 c.c. with toluene.

Octan-1-ol, mole	0·01	0·02	0·03	0·05	0·06	0·07	0·10	0·20
t, mins.	180	150	150	149	150	150	152	150
0·5N-NaOH, c.c.	5·8	6·4	6·9	7·5	7·3	7·1	6·9	6·6
Correction, c.c.	−0·2	−0·2	−0·2	−0·2	−0·1	−0·1	±0·0	+0·2
$k \times 10^4$	1·60	2·13	2·31	2·52	2·50	2·44	2·39	2·35

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