469. *Acid-catalysed Alcoholysis. Part III. Polar Solvents.*

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The effect of the addition of polar compounds to the acid-catalysed alcoholysis reaction in toluene has been further studied, and the methods used in Part II have been modified to permit of the use of some polar compounds as solvents.

The reduction of reaction velocity on the addition of polar compounds to the aprotic solvent has been confirmed and explained on the basis of hydrogen ion distribution between ester, alcohol, and added compound.

The great difference in reaction velocity when polar compounds are used as solvents has been shown to be quantitatively related to the proton affinity of the solvent.

It has been shown in Part I (this vol., p. 557) that the presence of an added polar compound during an acid-catalysed alcoholysis reaction in an inert solvent reduces the reaction velocity considerably. This was ascribed to the sharing of the hydrogen ion between the alcohol and the added polar compound. In Part II (preceding paper) a method was described which enabled the hydrogen ion distribution between the reagent alcohol and ester to be determined by varying the concentrations of the reagents, and it was shown that the equilibrium constant K_E for the reaction

$$R\cdot OH + EH^+ \rightleftharpoons R\cdot OH_2^+ + E \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where R·OH is octan-1-ol and E is ethyl acetate, is of the order 1·5.

For the alcoholysis reaction the basic velocity constant $-k_0$ was found to be $2{\cdot}0 \times 10^{-2}$ mol.l.$^{-1}$min.$^{-1}$ This constant is defined by the expression

$$V = k[CH_3\cdot CO_2Et] = k_0[CH_3\cdot CO_2Et]\alpha \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

where k is the observed velocity constant and α the alkyloxonium-ion concentration.

Having determined the relative affinity of the alcohol and the ester for the hydrogen ion, it was then possible to calculate the distribution on adding a polar compound S to the system. With the assumption made in Part II, the sytem is defined by equation (1) and the equation

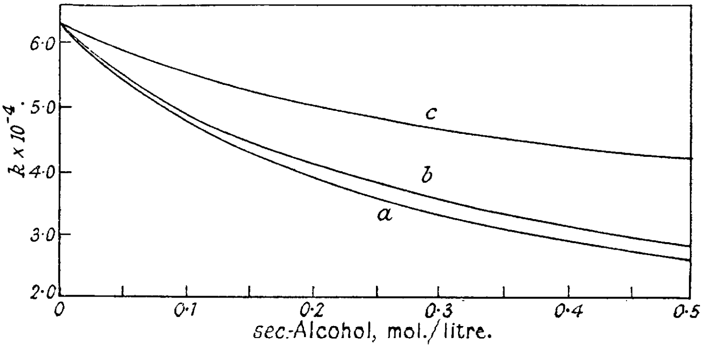
$$\mathrm{S} + \mathrm{R{\cdot}OH_2}^+ \rightleftharpoons \mathrm{R{\cdot}OH} + \mathrm{SH}^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (3)$$

A third relation between E and S is implicit in (1) and (3).

If the alcohol and ester concentrations are large in comparison with the catalyst concentration, the equilibrium constant K_S for reaction (3) is given by

$$K_S = \frac{(p - \alpha)\{c - \alpha(1 + e/PK_E)\}}{\alpha\,.\,[s - \{c - \alpha(1 + e/PK_E)\}]} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (4)$$

where p, e, c, and s are the initial concentrations of the alcohol, ester, catalyst, and added polar compound, respectively. From (2), $\alpha = k/k_0$, and, since K_E and k_0 are known, the value of K_S for any non-esterifiable compound added to the system can be calculated by substituting the observed value of α in (4). If the aprotic solvent can be regarded as a diluent only, on its replacement by a more polar compound, equation (4) should still apply and the value of K_S should be the same. This was found to be substantially true.



The method used for determining the reaction velocity was the same as in Part II when toluene was used, but when acetone was substituted as solvent a modification was necessary. Before evaporation of the solvent and low-boiling ester, toluene was added to facilitate the removal of the ester. In this case the ester is not removed so rapidly, but owing to the lower temperature reached by the evaporation of the acetone under a high vacuum, the reaction is effectively stopped. This source of error is also compensated to some extent, as the reaction velocity is much less in polar solvents and the time interval is consequently greater, so that the time interval error is small and usually less than 1%. With solvents that can be salted out the washing method can be used, provided that an extractive solvent is also used.

The number of polar solvents which can be employed is small and in practice is limited to ethers and ketones, although *tert.*-butanol was also used, as the amount of esterification, if any, is very slight and does not affect the result. This alcohol, acetone, and dioxan were chosen as they are easy to obtain in a very pure condition. These solvents are also not appreciably affected by the catalyst under the conditions of the experiment. In each case tests were made to verify this by examining a solution of the catalyst after a period of storage at room temperatures.

The variation of the observed rate constant k with three added secondary alcohols is shown in the figure. The curves refer to *iso*propanol (*a*), octan-2-ol (*b*), and phenylmethylcarbinol (*c*) at 0·05 mol./l. octan-1-ol and ester, 0·05 mol./l. catalyst, and variable amounts of added secondary alcohol in toluene at 25°. It will be seen that the curve for octan-2-ol is similar to that shown in Part I for the irreversible method.

An example of the constancy of K_S with varying concentrations of added polar compounds is shown in Table III. In this and other cases K_S is fairly constant over a wide range, but at low concentrations, *i.e.*, $<0{\cdot}025$ mol./l. of added polar compound, the experimental error in the evaluation of k is comparable with the expected difference in the rate and reliable results cannot be obtained. In the evaluation of K_S no account has been taken of the contribution to the total ester value owing to the presence of the esterifiable secondary alcohols. As was shown in Part I, this effect is quite small; the actual values are $k/c = 12{\cdot}4 \times 10^{-3}$ and $0{\cdot}8 \times 10^{-3}$ for octan-1- and -2-ol, respectively. However a slightly increased value of α will be given for a non-volatile alcohol and a decreased value for a volatile one. Hence the recorded value of K_S will be slightly too high for *iso*propanol and too low for octan-2-ol.

For the system, 0·5 mol./l. each of ethyl acetate, octan-1-ol, and added polar compound, and 0·05 mol./l. of catalyst in toluene at 25°, the values of K_S are: *tert.*-butanol 3·8, α-terpineol 2·8, *iso*propanol 2·4, octan-2-ol 2·0, phenylmethylcarbinol 0·76, acetone 0·50, dioxan 0·45. Also, since $K_E = 1·5$, the reference substance, octan-1-ol, is 1·0 and ethyl acetate 0·67. The value of K_S for phenols cannot be determined by this method as the presence of the phenol affects the titration end-point, but an approximate value can be given for *m*-cresol, which from Part I would be 0·33.

TABLE I.

Solvents: (*a*) acetone, (*b*) dioxan, (*c*) *tert.*-butanol.

(*a*) Octan-1-ol, mols./l.	1·0	1·5	2·0
s, mols./l.	10·3	9·2	8·1
$k \times 10^4$, min.$^{-1}$	1·14	1·70	2·46
K_S	0·62	0·64	0·59
(*b*) Octan-1-ol, mols./l.	1·0	1·5	2·0
s, mols./l.	8·75	7·9	6·93
$k \times 10^4$, min.$^{-1}$	1·48	2·06	2·49
K_S	0·58	0·64	0·68
(*c*) Octan-1-ol, mols./l.	0·5	1·0	2·0
s, mols./l.	9·15	8·05	6·35
$k \times 10^5$, min.$^{-1}$	1·63	2·13	4·25
K_S	3·3	5·6	7·0

The variation of K_S for measurements in polar solvents is shown in Table 1. In each case the ethyl acetate concentration is 1·0 mol./l. and the catalyst concentration 0·05 mol./l., with varying amounts of octan-1-ol at 25°. The value of s is the number of mols. of solvent required to make up 1 l. of solution. For dioxan the unit is the molecular weight and not the equivalent.

The agreement between the values obtained for K_S when the polar compound is added to the toluene system and when used as a solvent is good having regard to the difference in experimental conditions and the assumptions made. The results with the polar solvents are not so accurate as with the toluene system where the added polar compound concentration can be measured with greater accuracy. The high values for K_S obtained with *tert.*-butanol as solvent are noteworthy and are probably due to increased ion association at the high concentration of octan-1-ol employed.

In contrast to the large reduction in the rate constant by the addition of polar compounds in an aprotic solvent as shown in the figure the reduction is small when polar compounds are added to the polar solvent system. This is shown in Table II, which also summarises the reaction velocities for the alcoholysis reaction in various solvents under the same conditions. Concentrations are 1·0 mol./l. for ethyl acetate, octan-1-ol, and added compound, and 0·05 mol./l. for the catalyst. The temperature was 25° ± 0·1°.

TABLE II.

Solvent.	Added compound.	$10^3k/c$ & max. deviation from mean.
*iso*Octane	Nil	13·0 ± 0·4
Toluene	Nil	12·4 ± 0·4
Toluene	Octan-2-ol	5·4 ± 0·3
Acetone	Nil	2·28 ± 0·1
Acetone	Octan-2-ol	2·10 ± 0·1
Acetone	*tert.*-Butanol	1·88 ± 0·1
Dioxan	Nil	2·96 ± 0·15
Dioxan	Octan-2-ol	2·86 ± 0·15
Dioxan	*tert.*-Butanol	2·46 ± 0·15
tert.-Butanol	Nil	0·43 ± 0·05

The small but significant difference in the values of k/c for toluene and *iso*octane shows that the former possesses some affinity for the hydrogen ion, and the latter should have been used as solvent, but the solubility of the catalyst is less in *iso*octane and exhibits a tendency to deposit from solution when small concentrations of octanol are used. The assumption that toluene is a completely aprotic solvent introduces a source of error, but this cannot be accurately determined as the proton affinity is too small significantly to affect the experimental data.

The values of K_S are a measure of the proton affinity or basicity of the added polar compound, and, as stated in previous work, the dielectric constant of the substrate is not an important factor, the results being accounted for on the basis of the hydrogen ion sharing by the polar compounds in the system. Since Part I was accepted for publication, some work has been published (Braude, *J.*, 1948, 1971; Braude and Stern, *ibid.*, pp. 1976, 1982) in which the authors of the third paper have arrived at the same conclusion for an acid-catalysed anionotropic rearrangement, and the present work may be considered as confirmation of their views. In the first paper Braude also measured the acidity function for a group of solvents and concluded that the basicities or proton affinities were in the order water > dioxan > ethanol > acetone. Obviously, water or ethanol cannot be compared directly in the alcoholysis reaction as described in this paper, but if it is assumed that K_S for ethanol is $\simeq 1$, the value for the standard octan-1-ol, then the order is ethanol > acetone > dioxan. Braude, from a consideration of electron availability alone, assumes that the order should be ether > ethanol > acetone, but there are other factors to be taken into account. Whereas in the present work the ionization of the catalyst may be regarded as practically complete owing to the presence of a large concentration of reagents in the otherwise non-ionizing solvents, Braude shows that the ionization of hydrochloric acid in dioxan is small, and the low concentration of reagents that he used would not increase the ionization appreciably.

EXPERIMENTAL.

Materials.—The preparation of most of the materials used has been previously described. The remainder were low-boiling solvents which were selected on account of their original purity. The *tert.*-butanol was crystallised to constant m. p.; the *iso*propanol and dioxan were distilled over sodium, and the acetone was treated with permanganate. All the above were distilled, middle fractions only being used.

Method.—The catalyst solution was made up as follows. The catalyst was dissolved in the octan-1-ol, benzene added, and the water removed by azeotropic distillation. The benzene was completely removed under high vacuum, and the residue was made up to the required dilution with the polar solvent to be used.

When acetone was used as solvent the direct procedure of Part II was applied with the following modification. After applying vacuum to remove the solvent and stop the reaction, 50 c.c. of chilled toluene were added to serve as entrainant for removing the last trace of ethyl acetate.

With dioxan and *tert.*-butanol as solvents, the washing procedure was used with some modification. To stop the reaction, the contents of the reaction tube were poured on to 100 c.c. of toluene and 50 c.c. of a standard sodium hydrogen carbonate solution containing 200 g./l. of sodium chloride, and the mixture shaken vigorously. The aqueous layer was removed, and the top layer shaken with 25 c.c. of 20% brine. The non-aqueous portion was evaporated, and the ester determined as previously described.

The control tests were carried out as described in Part II and applied in the same manner. With acetone and toluene as solvent there is a negative correction, but with dioxan and *tert.*-butanol there is a somewhat large positive correction.

An example of the results obtained and the data employed in calculating K_S is given in the following table where the concentrations are: ethyl acetate and octan-1-ol, 0·5 mol./l., *m*-xylenesulphonic acid, 0·05 mol./l., with varying amounts of octan-2-ol in toluene at 25°. $K_E = 1{\cdot}5$ and $k_0 = 0{\cdot}02$ mol.l.$^{-1}$min.$^{-1}$

TABLE III.

Octan-2-ol, mols./l.	0	0·025	0·05	0·10	0·25	0·5
N-NaOH, c.c.	8·25	9·1	7·1	6·55	5·25	3·8
Correction, c.c.	−0·4	−0·45	−0·35	−0·30	−0·40	−0·25
t, mins.	135	162	133	136	132	135
$k \times 10^4$	6·32	5·86	5·45	4·83	3·83	2·73
K_S	—	0·81	1·76	1·98	1·95	2·04

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