

375. *Polar and Non-polar Effects in Esterification.*

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THE esterification of a carboxylic acid involves the bond ruptures $R\cdot COOH$ and $R'O\cdot H$. If the reaction is catalysed by undissociated molecules of the reacting acid, then there is a proton transfer involving the rupture $R\cdot COO\cdot H$. The two processes occurring in the acid will be oppositely influenced by polar substituents, and it is difficult to predict whether the substituents will increase or decrease the rate of reaction. Actually, trichloroacetic acid reacts with benzyl alcohol more readily than acetic acid, and the corresponding energy of activation is about 2000 calories lower (Hinshelwood and Legard, this vol., p. 587). When the catalyst consists of hydrions, *e.g.*, from added hydrogen chloride, this compensation will not occur, and the polar effect of the substituents should be more clearly marked. Hence, it appeared useful to supplement the series of reactions previously studied by the series : acetic acid, trichloroacetic acid, trimethylacetic acid, with hydrogen chloride as catalyst and with a given alcohol. Ethyl alcohol had to be chosen, since benzyl alcohol reacts too rapidly with hydrogen chloride, and the methyl ester of trichloroacetic acid is so readily hydrolysed that it is impossible to follow the reaction in methyl alcohol by the ordinary alkali titration method, even using ammonia.

It is known from the work of Sudborough and Lloyd (J., 1899, **75**, 467) that under the influence of hydrogen chloride trichloroacetic acid reacts with ethyl alcohol much more slowly than acetic acid. The energy of activation of the reaction has not been determined, however, and it is doubtful whether previous measurements have separated the contributions to the total reaction of the hydrion-catalysed and the autocatalytic process. This separation happens to be rather difficult in the present case. Trimethylacetic acid was also found by Sudborough and Lloyd to be esterified much more slowly than acetic acid.

This is the reverse of what might be expected from the polar effects of the methyl groups, a fact which adds interest to the determination of the activation energy.

The following table summarises the important results. The data are, we believe,

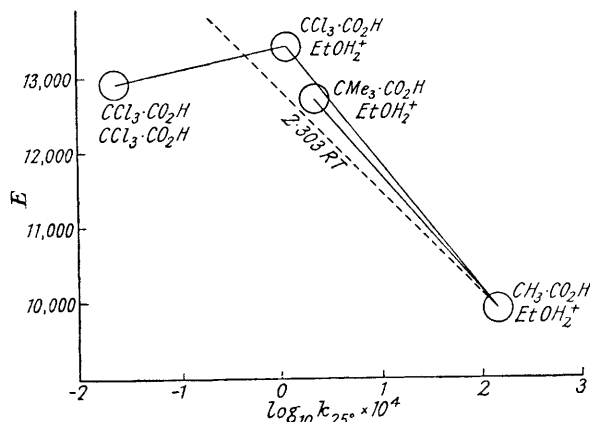
Acid.	Catalyst.	<i>E.</i>	<i>k</i> at 25°.	Acid.	Catalyst.	<i>E.</i>	<i>k</i> at 25°.
CH ₃ ·CO ₂ H	EtOH ₂ ⁺	9,900	1.48 × 10 ⁻²	CCl ₃ ·CO ₂ H	EtOH ₂ ⁺	13,400	1.14 × 10 ⁻⁴
CMe ₃ ·CO ₂ H	EtOH ₂ ⁺	12,700	2.19 × 10 ⁻⁴	CCl ₃ ·CO ₂ H	CCl ₃ ·CO ₂ H	12,900	2.16 × 10 ⁻⁶

significant, and comparable among themselves for our present purpose, but for practical reasons those for trichloroacetic acid cannot be of the highest degree of accuracy.

The conclusions to be drawn from the table are :

(1) The autocatalytic esterification of trichloroacetic acid is very much slower than the hydron-catalysed reaction in spite of the fact that the activation energy is no greater. This provides another example of the fact that the factor *P* (see this vol., p. 587) is much greater for the reaction involving the charged catalyst.

(2) The hydron-catalysed reaction of trichloroacetic acid is much slower than that of acetic acid, and the activation energy is correspondingly higher. This is what would be expected from the polar effect of the chlorine atoms in making the detachment of the hydroxyl group from the acid more difficult.



(3) The hydron-catalysed reaction of trimethylacetic acid is much slower than that of acetic acid, and the activation energy is also higher; but these two effects are the opposite of what might be expected from the polar influence of the methyl groups, which lower the dissociation constant of the acid, and might therefore be expected to facilitate the splitting off of the hydroxyl group. The increase in activation energy and the reduction of reaction velocity must therefore depend upon an influence of the methyl groups which cannot appropriately be called polar. It is of interest to note that this influence operates on *E*, and not simply on the factor *P*.

(4) The fact that methyl groups and chlorine atoms both reduce the rate of esterification has sometimes been taken to indicate that neither influence is a polar one. It seems clear that with trimethylacetic acid the effect is of another kind, but we are inclined to think that the principal action of the chlorine atoms in trichloroacetic acid is, in fact, a polar one for the following reason. When the reaction is catalysed by trichloroacetic acid itself, it is faster than the reaction of the unsubstituted acid, on account of the compensating effect discussed above. The easiest way to interpret the compensation is in terms of polar influences. It is quite reasonable to assume that polar effects predominate in trichloro- but not in trimethyl-acetic acid: the dissociation constant of the latter is of the order of only ten times smaller than that of acetic acid, whereas that of the trichloro-acid is thousands of times greater.

The relative importance of changes in *E* and in *P* in determining the variation of reaction rate is shown in the figure by the method described in our previous paper.

EXPERIMENTAL.

Trichloroacetic acid was purified by distillation, and acetic acid by repeated freezing. Trimethylacetic acid, for which we are indebted to Mr. T. W. J. Taylor, had been fractionated in a vacuum, and was further purified by fractional crystallisation from the melt. The alcohol had been dehydrated for conductivity work, though the extremely hygroscopic nature of the solutes makes it doubtful whether the initial solutions were absolutely anhydrous. Every care was, however, taken to minimise the absorption of water vapour. Buffer solutions containing sodium trichloroacetate were made by adding standardised solutions of sodium ethoxide to the acid.

With acetic acid and trimethylacetic acid, the only reaction occurring under the conditions of the experiments is the hydrion-catalysed reaction, and the concentration of the hydrion can be taken without appreciable error as that of the added hydrogen chloride. Goldschmidt's formula can be applied for the calculation of the velocity constants (for formulæ, see *Trans. Faraday Soc.*, 1934, **30**, 1145). The values of ν adopted were as follows: 0°, 0.05; 20°, 0.09; 40°, 0.15; 60°, 0.26. (These are smaller than the corresponding values for methyl alcohol, which means that the retarding action of water is more serious with ethyl alcohol; *i.e.*, that ethyl alcohol competes less effectively than methyl alcohol for the hydrions. It must be remembered, however, that ν is a very sensitive constant, and that it would be infinite in the case of no retardation by water. Small changes in the reaction-time curve mean large changes in ν , and conversely, a very rough value of ν is all that is needed to give quite good velocity constants. Thus the difference between methyl and ethyl alcohol in this respect is less marked than it might seem.)

With trichloroacetic acid, several difficulties arise. First, the ethyl ester is rapidly hydrolysed by alkali. To follow the reaction, therefore, the solutions were rapidly titrated with standard ammonia solution, methyl-red being used as indicator. Secondly, the reaction is much more complex kinetically. There is a considerable contribution from the autocatalytic reaction even in presence of hydrogen chloride, and in the absence of hydrogen chloride there is a considerable contribution from the hydrion-catalysed reaction, the dissociation of trichloroacetic acid in alcohol, though small, being appreciable.

Hence, neither of the constants in the equation

$$-d[\text{HX}]/dt = k_0[\text{HX}][\text{ROH}_2^+] + k_1[\text{HX}]^2$$

can be isolated by a direct experiment. The method adopted for obtaining them was as follows.

(1) The rate of reaction was measured in presence of buffer solutions containing 0.40*N*-trichloroacetic acid and 0.01*N*-, 0.05*N*-, or 0.1*N*-sodium salt. In all these the hydrion concentration could be taken as negligible. The catalytic effect of the buffer at the two higher concentrations was small enough to allow the reaction rate in presence of 0.01*N* buffer to be regarded as approximately that of the autocatalytic reaction, and the corresponding bimolecular constants were calculated, and taken as provisional values of k_1 . From the constants the initial rate of reaction was calculated.

(2) Curves were next plotted for initial rates (as found by tangents in each run) against [HCl], and extrapolation of these to [HCl] = 0 yielded values in approximate agreement with those found in (1), the hydrogen chloride having repressed the ionisation of the trichloroacetic acid. By drawing the best straight line through all the points, including that found in (1), approximate values of k_0 and k_1 could be determined. This is the best we can do for k_1 , but the results are reasonably reliable since the values obtained from (1) and (2) check.

(3) Rather more accurate values for k_0 are now found as follows. The above equation is integrated, giving

$$t = \frac{2.303}{k_0 c} \log \frac{a\{(a-x) + Kc\}}{(a-x)\{a + Kc\}}$$

where a is the initial concentration of the acid, c that of the hydrogen chloride, and $K = k_0/k_1$. For K we use the provisional values found in (2). A series of values of k_0 are now calculated from the values of x and t for the experiments in presence of hydrogen chloride. The values found are not constant but fall with increasing x , since the equation only holds for the initial rate, k_0 diminishing as water is formed, in accordance with Goldschmidt's formula. Finally, therefore, the series of k_0 values are plotted against x and extrapolated to zero. The result is taken as the final value for k_0 .

Trichloroacetic acid.

Temp.	[HCl].	$k_0 \times 10^4$.	$k_0 \times 10^4$, mean.	$k_1 \times 10^6$.		Mean.
				By extra- polation.	From 0.01N- buffer.	
60.0°	0.02	10.6	10.6	21.5	21.3	21.4
	0.01	10.5				
	0.005	10.9				
50.4	0.02	7.05	6.97	10.2	11.2	10.7
	0.01	6.90				
42.7	0.02	4.26	4.32	5.95	6.77	6.36
	0.01	4.52				
	0.005	4.18				
35.6	0.02	2.13	2.36	3.43	3.10	3.26
	0.01	2.27				
	0.005	2.69				
25.0	0.02	1.33	1.14	1.95	2.38	2.16
	0.015	1.11				
	0.010	1.00				

The values given in the foregoing table satisfy the Arrhenius equation as well as can be expected when the inherent difficulties are taken into account.

Trimethylacetic acid.

$$a = 0.200.$$

Temp.	60.4°	45.3°	25.7°	0.2°
Mean $k \times 10^4$	21.0	7.85	2.26	0.264

Acetic acid.

Temp.	50.0°	45.3°	37.1°	25.1°
Mean $k \times 10^3$	53.2	42.4	30.5	14.75

For acetic and trimethylacetic acids the Goldschmidt formula and the Arrhenius equation are both well satisfied, but no very elaborate series of measurements was made to ensure the maximum possible accuracy since the results were only needed for comparison with those for trichloroacetic acid, where the nature of the problem made the highest accuracy unattainable.

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