The Effect of Substituents and α,β -Unsaturation on the Alkaline Hydrolysis of α,β -Unsaturated Aliphatic Esters

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The alkaline hydrolysis of the ethyl esters of propiolic, tetrolic and *tert.* butylpropiolic acids has been studied in the temperature range 0–40° C in water (only the first two esters) and acetone-water mixtures. The rate constants of the alkaline hydrolysis of the first two esters in water at 25° C are 4.68 and 0.568 l mole⁻¹sec.⁻¹ and those for the three esters in 50 wt. % acetone-water 1.302, 0.1139 and 0.0481, respectively. The activation energies for these esters are approximately 1500 cal. higher than those of the corresponding saturated esters, and hence the approximately fifty times higher rates of the former esters are due to high values of the Arrhenius frequency factor. By comparing the rates of the alkaline hydrolysis of various saturated, α,β -ethylenic and α,β -acetylenic esters, it has been concluded that the effects of substituents in the latter two groups of esters are primarily due to conjugative effects which lead to the higher differences in the rates of the unsaturated esters compared with those of the corresponding saturated esters.

The unsaturated bonds in α,β -unsaturated esters may be expected to effect a pronounced increase in the rate of alkaline hydrolysis of these esters owing to their electronegativity but a decrease in this rate by virtue of conjugation with the carboxyl carbonyl group. In addition, substituents at the outer end of the unsaturated bond may influence the rate by an inductive, conjugative or hyperconjugative effect. Since it is not possible to distinguish between these effects by a study of the rates of alkaline hydrolysis of α,β -ethylenic and saturated aliphatic esters alone, the alkaline hydrolysis of several α,β -acetylenic esters has been investigated to obtain more information on the interplay of these various factors.

EXPERIMENTAL

Ethyl propiolate. 16 g of propiolic acid prepared as described previously¹ were dissolved in 60 ml of absolute alcohol containing 5 g of concentrated sulphuric acid. After the mixture had stood at room temperature for 60 hours, water was added and the ester formed extracted with ether. The ether solution was washed with sodium bicarbonate

solution and dried with calcium chloride, after which the solvent was evaporated. The ester was distilled by fractionation in a Widmer column. Its b.p. was 120.0° C at 760 mm Hg. The yield was 9.15 g (40 % of theory). The ester was a clear liquid with a pungent odour which strongly irritated the eyes and skin.

Ethyl tetrolate. This ester was prepared from previously synthesized tetrolic acid¹ by the preceding method except that the reaction mixture was heated on the water bath for one hour. The ester boiled at 164.5–165.0° at 760 mm Hg. The yield was 64 % of the theoretical. The odour of the ester resembled that of ethyl propiolate, but was less intense and less disagreeable.

Ethyl tert. butylpropiolate. This ester was obtained by esterification of previously prepared *tert.* butylpropionic acid² according to the method given above for ethyl propiolate, but with the difference that the reaction mixture was boiled two hours on the water bath and the ester distilled under diminished pressure. B. p. 83.0–83.5° C at 23 mm Hg. The yield was 95 % of the theoretical. The ester had a weak pleasant odour.

Total saponification tests conducted on these esters gave a purity of 100 % within the limits of experimental accuracy, in view of which they were sufficiently pure for kinetic measurements.

Acetone (pro analysi, Merck) and sodium hydroxide (reagent grade, Baker) were used as such. The water employed was ordinary distilled water.

Kinetic measurements. The hydrolyses were conducted in three-necked reaction flasks³. Seven samples were titrated in each experimental run at each temperature. The concentrations of sodium hydroxide and ester were both 0.01 *M* in the initial mixture and the sample volume 10 ml. After appropriate intervals, the reaction was arrested by adding an excess of 0.02 *N* hydrochloric acid, and the excess of acid was titrated with 0.02 *N* barium hydroxide using cresol red as indicator.

From the total saponification values it was concluded that the triple bonds do not add water at the temperatures employed. The esters did not hydrolyse in water or dilute hydrochloric acid during several days at room temperature.

RESULTS

The experimental data are collected in Table 1. The rate constants have been computed from the usual second order rate equation. The activation energies and frequency factors were calculated by the method of least squares. The rate constants were found to decrease approximately 5 % in the experimental run when the reaction progressed from 20 to 70 % saponification. The decrease in the values of the rate constants increased with temperature and with the water content of the solvent. Since the total saponification gave an approximately 100 % reaction, the decrease in the rate constant is evidently due to the evaporation of the ester into the gas phase in the reaction flask.

Table 1. Kinetic data on the alkaline hydrolysis of ethyl propiolate, tetrolate, and *tert.* butylpropiolate in water and in acetone-water mixtures.

Reactant	Solvent composition wt % H ₂ O	<i>k</i> l mole ⁻¹ sec. ⁻¹					<i>E</i> cal.	log <i>A</i>
		0°	13.00°	15.00°	32.00°	40.00°		
HC≡C·CO ₂ Et	100	0.661	1.93	4.68	7.33	11.7	12 260	9.638
—»—	80	0.637	1.62	3.54	5.13	8.06	10 780	8.435
—»—	50	0.235	0.572	1.30	2.09	3.35	11 360	8.448
CH ₃ ·C≡C·CO ₂ Et	100	0.0761	0.229	0.568	0.901	1.51	12 710	9.055
—»—	80	0.0633	0.159	0.355	0.545	0.859	11 120	7.699
—»—	50	0.0178	0.0475	0.114	0.182	0.298	12 030	7.868
(CH ₃) ₂ C=C≡C·CO ₂ Et	50	0.00716	0.0197	0.0481	0.0808	0.138	12 590	7.920

DISCUSSION

In Table 2 are given the specific rates at 25° C, the activation energies and frequency factors for the alkaline hydrolysis of the ethyl esters of the α,β -acetylenic (excluding *tert.* butylpropionic ester since the corresponding saturated and α,β -ethylenic esters have not been studied kinetically), α,β -ethylenic acids and corresponding saturated acids in aqueous solution.

Table 2. The rate constants, activation energies and frequency factors for the alkaline hydrolysis of the ethyl esters of some saturated and α,β -unsaturated acids in water.

Reactant	k_{25}°	E cal.	$\log A$
$\text{H}_3\text{C} \cdot \text{CH}_2\text{CO}_2\text{Et}^4$	0.0870	10 720	6.780
$\text{H}_3\text{C} \cdot \text{CH}_2 \cdot \text{CH}_2\text{CO}_2\text{Et}^4$	0.0383	10 320	6.142
$^-\text{OOC} \cdot \text{CH}_2 \cdot \text{CH}_2\text{CO}_2\text{Et}^5$	0.0177	11 050	6.35
$\text{EtO}_2\text{C} \cdot \text{CH}_2 \cdot \text{CH}_2\text{CO}_2\text{Et}^5$	0.207	11 240	7.55
<i>trans</i> :			
$\text{H}_3\text{C} = \text{CH} \cdot \text{CO}_2\text{Et}^6$	0.0779	11 950	7.638
$\text{H}_3\text{C} \cdot \text{HC} = \text{CH} \cdot \text{CO}_2\text{Et}^6$	0.0130	12 720	7.431
$^-\text{OOC} \cdot \text{HC} = \text{CH} \cdot \text{CO}_2\text{Et}^6$	0.158	11 120	7.375
$\text{EtO}_2\text{C} \cdot \text{HC} = \text{CH} \cdot \text{CO}_2\text{Et}^6$	4.47	11 600	9.159
<i>cis</i> :			
$\text{H}_3\text{C} = \text{CH} \cdot \text{CO}_2\text{Et}^6$	0.0779	11 950	7.638
$\text{H}_3\text{C} \cdot \text{HC} = \text{CH} \cdot \text{CO}_2\text{Et}^7$	0.0146	—	—
$^-\text{OOC} \cdot \text{HC} = \text{CH} \cdot \text{CO}_2\text{Et}^6$	0.00486	13 390	7.502
$\text{EtO}_2\text{C} \cdot \text{HC} = \text{CH} \cdot \text{CO}_2\text{Et}^6$	0.407	11 500	8.064
$\text{HC} \equiv \text{C} \cdot \text{CO}_2\text{Et}$	4.68	12 260	9.638
$\text{H}_3\text{C} \cdot \text{C} \equiv \text{C} \cdot \text{CO}_2\text{Et}$	0.568	12 705	9.055
$^-\text{OOC} \cdot \text{C} \equiv \text{C} \cdot \text{CO}_2\text{Et}^8$	2.40	11 380	8.71
$\text{EtO}_2\text{C} \cdot \text{C} \equiv \text{C} \cdot \text{CO}_2\text{Et}^8$	69.0	10 900	9.84

It will be noted that the rates of the α,β -acetylenic esters are much higher than the rates of the corresponding α,β -ethylenic and saturated esters. As compared with the propionic ester, the acrylic and propiolic esters are characterized by a $-I$ effect of the unsaturated bond and conjugation between the latter and the carboxyl carbonyl group. Although conjugation is not probably very marked in unsaturated acids⁹, it is much greater in their esters since the conjugation energy of the carbalkoxyl group is approximately 4 000 cal. smaller than that of the carboxyl group in the acid¹⁰. In the acrylic ester the decrease in the rate caused by the conjugation overweighs the weak rate-promoting inductive effect of the sp^2 valence type of the double bond, and consequently the rate of this ester is smaller than that of the propionic ester. This conjugation is of the same magnitude in both propiolic and acrylic esters since only one p-electron pair can conjugate with a carbonyl group. In the triple bond the valence type is sp and accordingly its inductive effect is approximately a hundred times as great as that of a double bond. It is, however, surprising that although, as expected, the rate of the propiolic ester is nearly

60 times as great as the rates of the propionic and acrylic esters, the activation energy for the former ester is about 1 500 cal. higher than that of the propionic ester and of the same magnitude as that of the acrylic ester. (The energy difference is perhaps too great if, as suggested by Tommila ⁴, hydrogen bonding between the terminal methyl group and the carbonyl oxygen contributes to the activation energy in case of hydrolysis of the saturated esters). Hence it is not even approximately true that the activation energy of the ester is proportional to the dissociation constant of the corresponding acid, since the dissociation constant of propionic acid at 25° C is 1.33×10^{-5} ; that of acrylic acid 5.56×10^{-5} and that of propiolic acid about 500×10^{-5} . On the other hand, the activation energy appears as a rule to be proportional to the dissociation constant in a homologous series of acids, but this is no longer true for several series of acids. Since the activation energies for the propiolic and acrylic esters are nearly equal, their higher activation energy as compared with that of the propionic ester is evidently due to the conjugation between the unsaturated bond and the carboxyl carbonyl group, but the observed difference in the activation energies cannot readily be explained on the basis of generally accepted views on the mechanisms of alkaline ester hydrolysis ^{9,11}.

In the series of butyric, *trans*-crotonic and tetrolic esters, the methyl group introduces a $+I$ effect and in the crotonic ester there is π_y -hyperconjugation and in tetrolic ester a π_y - and π_z -hyperconjugation. From Table 1 we see that the rates of the ethyl esters of propiolic, tetrolic and *tert.* butylpropiolic acids in 50 % acetone-water at 25° C are 1.30, 0.114 and 0.0481 l mole⁻¹ sec⁻¹. The ratios of these rates are about 11 and 2.4, which indicates that the difference in the rates for the propiolic and tetrolic esters is due mainly to hyperconjugation. Hyperconjugation does not naturally exert as great a retarding effect on the alkaline hydrolysis of tetrolic ester as on the decarboxylation of tetrolic acid ¹², since it acts partly inductively in the former case. The ratio of the rates of hydrolysis of the propiolic and tetrolic esters is about 8 in water and about 11 in 50 % acetone-water at 25° C while the ratio of the decarboxylation rates of the anions of the acids in highly non-polar solvents is approximately 34 at 106.78° C. A similar view of the effect of the methyl group on the rates of the alkaline hydrolysis of α,β -unsaturated esters is obtained when the ratios of the rates of the following pairs of esters are compared: propionic-butyric, acrylic-*trans*crotonic and propiolic-tetrolic; the ratios are in water at 25° C 2.27, 5.99 and 8.23, respectively. The ratios thus increase with the degree of hyperconjugation. If the inductive effect alone determined the reaction rates, no greater differences would be observed between the ratios. The last ratio is smaller than would be expected if the effects were additive, but it seems natural that the effect of hyperconjugation ($+I$) on the reaction rate is relatively smaller in relation to the strong inductive effect of the triple bond than to the weak inductive effect of the double bond. Since the rate of hydrolysis of the ethyl ester of *cis*-crotonic acid is almost as large as that of the *trans*-crotonic ester, although conjugation presumably is not possible in the former, it must be concluded that a strong steric effect operates in the *cis*-crotonic ester.

The carboxylate ion group is electropositive by nature ^{9,12}, also when it is attached to an unsaturated bond, since the internal resonance, about 36 000

Fig. 1. The logarithm of the rate constant as a function of bond order for the alkaline hydrolysis of the ethyl esters of some saturated and α,β -unsaturated acids in water. The points joined by broken lines refer to esters of *cis* acid.

cal.¹⁰, of the group is so large that it does not enter into conjugation with a neighbouring unsaturated bond. However, the carboxylate ion group is strongly solvated in water, the solvation energy being of the order of 6 000 cal.¹³. Consequently the negative charge is masked, as a result of which the inductive effect becomes more electronegative and also conjugation is favoured. The effect of the ionised carboxylate group in the ester hydrolysis of monoethyl succinate and monoethyl acetylenedicarboxylate (Table 2, Fig. 1) acts in the expected direction, *i. e.* the rates are smaller than those of the propionic and propiolic esters. The rate of hydrolysis of the fumaric ester ion, on the other hand, is about twice that of ethyl acrylate in water, but the ratio decreases when an organic solvent is added to the solvent, being 1.26 in 58.3 % ethanol-water, and it is possible that the ratio will decrease below unity as the solvent becomes less polar. Also the change in the activation energy with the composition of solvent in ethanol-water and dioxan-water mixtures is greater for the fumaric ester ion than for diethyl fumarate⁶, which may also be due to the solvation of the carboxylate ion group. Also the reaction rates, activation energies and frequency factors of the *m*- and *p*-phthalic ester ions are approximately equal, the rates in water being approximately twice that of ethyl benzoate¹⁴.

The rates of hydrolysis of the diethyl esters of fumaric and acetylenedicarboxylic acids are clearly greater than the rate of diethyl succinate. In unsaturated esters the main effect is the conjugative effect since the ratios of the rates of hydrolysis of esters of the acid pairs, succinic-propionic, fumaric-acrylic and acetylene-dicarboxylic-propionic are 2, 60 and 15. A similar weakening as that observed in the case of the hyperconjugative effect is noted in the conjugative effect in the acetylenic compounds as compared to the ethylenic compounds. If we compare the ratios of the rates for the ester pairs, diethyl- and monoethyl succinates, diethyl- and monoethyl fumarates and diethyl-

and monoethyl acetylenedicarboxylates, 11.7, 28.3 and 28.7, we find that these are exactly in accordance with the assumed variation of the conjugative effect. From Fig. 1 it will be seen that owing to conjugative effects of the substituents, larger differences exist between the rates of the esters of α,β -unsaturated esters than between the rates of saturated esters.

The solvent effect is normal for all esters studied^{15,4} the rate of alkaline hydrolysis decreases as the acetone content increases in acetone-water mixtures (Table 1), and a minimum in the activation energy, a depression of about 1 500 cal., is observed when the mixture contains approximately 20 % acetone.

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