Acid-catalysed Hydrolysis of Alkyl Benzoates

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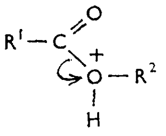
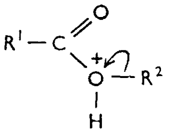
The kinetics of the hydrolysis reactions of several new isopropyl and methyl benzoates have been followed in concentrated sulphuric acid and in dilute oleum. Hammett $\sigma\rho$ plots are used to establish the $A_{Al}1$ and $A_{Ac}1$ mechanisms.

ESTERS of carboxylic acids undergo acid-catalysed hydrolysis reactions in aqueous sulphuric acid.[1-4] There are four possible mechanisms,[5] $A_{Ac}1$, $A_{Al}1$, $A_{Ac}2$, and $A_{Al}2$, but only the first three have been observed experimentally. The majority of esters in aqueous sulphuric acid hydrolyse by the bimolecular acyl-oxygen mechanism but in concentrated acid (80—100% sulphuric acid) the rate profiles for most acetates pass through a minimum,[6-8] and one of the unimolecular processes becomes operative at high acidities.



$A_{Ac}1$

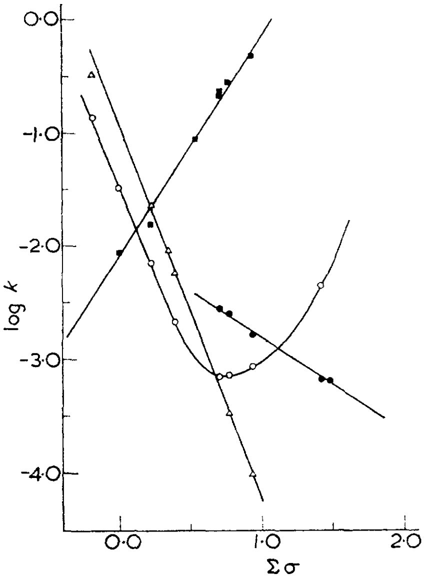


$A_{Al}1$

The $A_{Al}1$ mechanism can be equally well explained in terms of the experimentally observed carbonyl-protonated ester,[9] but ether protonation is essential for the $A_{Ac}1$ mechanism.

Kuhn[2] showed that the rate of the hydrolysis reaction for the unsubstituted benzoates in 100% sulphuric acid depended on the nature of the alkyl group R^2; the order was methyl $>$ ethyl $\ll$ isopropyl $<$ t-butyl. He concluded that the esters of secondary and tertiary alcohols hydrolyse by a different mechanism from those of primary alcohols. Graham[10] and Leisten[3] established that the rate of hydrolysis of methyl benzoate is independent of both the possible nucleophiles, water and hydrogen sulphate ion in the range 98% sulphuric acid to dilute oleum, thereby demonstrating that the reaction is a unimolecular decomposition of the protonated ester.

Kershaw and Leisten[11] used a cryoscopic method to follow the hydrolysis of a series of methyl and ethyl benzoates in 99·99% sulphuric acid. They used a Hammett $\sigma\rho$ plot to show that the methyl esters were all hydrolysed by the $A_{Ac}1$ mechanism and that the ethyl derivatives show a change of mechanism at high ρ values: strongly electron-withdrawing groups result in alkyl-oxygen fission (see Figure).



Hammett $\sigma\rho$ plots for the unimolecular acid-catalysed hydrolysis of alkyl benzoates; (—■—) isopropyl benzoates in 98·7% H_2SO_4, (—●—) methyl benzoates in 0·414m-$H[B(HSO_4)_4]$, (—△—) methyl benzoates in 99·99% H_2SO_4, (—○—) ethyl benzoates in 99·99% H_2SO_4

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In this work an attempt was made to observe alkyl-oxygen fission ($A_{\mathrm{Al}}1$) for methyl esters by using benzoates with strongly electron-withdrawing substituents, and the hydrolysis mechanism of the isopropyl benzoates was examined.

RESULTS AND DISCUSSION

The hydrolysis of the isopropyl benzoates could not be followed by the cryoscopic method,[11] owing to the rapidity of the reaction and the decomposition of one of the products, propan-2-ol. The latter reaction was found to be slower in more aqueous acid, and 98·7% sulphuric acid was used as solvent for the isopropyl ester work. Also the methyl benzoates studied were all very weak bases in 100% sulphuric acid, owing to their strongly electron-withdrawing groups, and it was decided to follow their hydrolysis in a much stronger protonating medium, a 0·4m-solution of tetra(hydrogen sulphato)-boric acid, $H[B(HSO_4)_4]$, in 100% sulphuric acid.[12] All the kinetics were followed by estimation of the remaining ester by use of a quantitative extraction method.

The rate constants and Hammett σ values for the methyl and isopropyl benzoates are given in Tables 1 and 2 and are shown in the Figure along with Kershaw and Leisten's data [11] for the methyl and ethyl benzoates. The ρ value for the hydrolysis of isopropyl benzoates is 1·991 (least-squares correlation coefficient 0·994) and for the methyl benzoates in oleum is −0·825 (correlation coefficient 0·995). The sign of the ρ value indicates whether the mechanism is $A_{\mathrm{Ac}}1$ or $A_{\mathrm{Al}}1$. Electron-withdrawing substituents assist alkyl-oxygen fission, since this mechanism requires movement of electrons towards the acyl group, R^1, of the ester and hence results in a positive ρ value. In acyl-oxygen fission electrons move away from the acyl group.

TABLE 1

Kinetic data for the hydrolysis of methyl benzoates at 64·8° in 0·414m-tetra(hydrogen sulphato)boric acid in 100% sulphuric acid

	Σσ [a]	$k \times 10^4$ (min.$^{-1}$)
Methyl 3-nitrobenzoate	0·71	27·1
Methyl 4-nitrobenzoate	0·778	25·1
Methyl 4-chloro-3-nitrobenzoate	0·937	15·9
Methyl 3,5-dinitrobenzoate	1·42	6·63
Methyl 3,4-dinitrobenzoate	1·488	6·53

[a] See ref. 13.

TABLE 2

Kinetic data for the hydrolysis of isopropyl benzoates at 0·0° in 98·7% sulphuric acid

Ester	Σσ [a]	$k \times 10^2$ (min.$^{-1}$)
Isopropyl benzoate	0	0·85
Isopropyl 4-chlorobenzoate	0·227	1·53
Isopropyl 4-methyl-3-nitrobenzoate	0·54	8·91
Isopropyl 3-methyl-4-nitrobenzoate	0·709	19·0
Isopropyl 3-nitrobenzoate	0·710	22·5
Isopropyl 4-nitrobenzoate	0·778	27·0
Isopropyl 4-chloro-3-nitrobenzoate	0·937	47·0

[a] See ref. 13.

The high correlation coefficients obtained for the least-squares treatment on the Hammett σρ plots show that only one hydrolysis mechanism can be prominent for each set of data. The low ρ value for the methyl benzoates hydrolysed in the tetra(hydrogen sulphato)-boric acid solution is caused by the high temperature and high dielectric constant [13,14] of the solvent, and we conclude that there is no evidence for alkyl-oxygen fission for methyl benzoates.

EXPERIMENTAL

Reagents.—The 0·414m-tetra(hydrogen sulphato)boric acid solution was prepared by addition of sufficient boron oxide to convert an oleum 1·242m in disulphuric acid quantitatively into a solution of tetra(hydrogen sulphato)-boric acid in 100% sulphuric acid.[12]

The concentration of the 98·7% sulphuric acid was accurately determined by electrical conductance measurement, with use of a calibration curve of conductance against percentage water in the sulphuric–water system.[15]

All the methyl esters were prepared by heating substituted benzoic acids under reflux with methanol and sulphuric acid. The esters were recrystallised from ethanol. All gave m.p.s in good agreement with literature values: methyl 4-nitrobenzoate 95° (lit.,[16] 95°); methyl 3-nitrobenzoate 79° (lit.,[17] 78·5°); methyl 3,4-dinitrobenzoate 86° (lit.,[18] 87°); methyl 4-chloro-3-nitrobenzoate 83° (lit.,[19] 83°); methyl 3,5-dinitrobenzoate 107° (lit.,[20] 107·8°).

Isopropyl benzoate was obtained commercially and purified by distillation, b.p. 218° (lit.,[21] 219°). The remaining isopropyl esters were all prepared by the method of Brewster and Ciotti.[22] The aromatic acid (1 mol.) was dissolved in dry pyridine, and toluenesulphonyl chloride (2 mol.) was added. The mixture was chilled in ice for several min., then propan-2-ol (1 mol.) was added. After a further 1 hr. the solution was poured into water to precipitate the ester, which was filtered off and recrystallised from ethanol. Isopropyl 4-nitrobenzoate had m.p. 109° (lit.,[22] 108—110°); *isopropyl 4-chloro-3-nitrobenzoate* gave yellow crystals, m.p. 64° (Found: C, 49·3; H, 4·1; Cl, 14·5; N, 6·25. $C_{10}H_{10}ClNO_4$ requires C, 49·1; H, 4·1; Cl, 14·5; N, 6·1%); *isopropyl 3-methyl-4-nitrobenzoate* gave yellow crystals, m.p. 60° (Found: C, 58·65; H, 5·95; N, 6·55. $C_{11}H_{13}NO_4$ requires C, 58·95; H, 5·8; N, 6·7%); *isopropyl 4-methyl-3-nitrobenzoate* gave pale yellow crystals, m.p. 59° (Found: C, 59·3; H, 6·0; N, 6·45. $C_{11}H_{13}NO_4$ requires C, 58·95; H, 5·8; N, 6·7%); *isopropyl 3-nitrobenzoate* gave an oil, purified by extracting an ethereal solution with aqueous sulphuric acid, evaporating off the ether, and drying under

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vacuum (Found: C, 57·3; H, 5·3; N, 7·05. $C_{10}H_{11}NO_4$ requires C, 57·1; H, 5·2; N, 7·1%); *isopropyl 4-chlorobenzoate* gave an oil (Found: C, 60·3; H, 5·6; Cl, 18·0. $C_{10}H_{11}ClO_2$ requires C, 60·5; H, 5·5; Cl, 17·9%).

Kinetic Method.—The kinetics of the hydrolysis reactions were followed by removing samples (5 ml.) from the reaction vessel at suitable times and pouring them into a slurry of rapidly stirred sodium hydrogen carbonate in ice-cold water (100 ml.). The concentration of the slurry was such that the final solution was saturated. The ester was extracted by ether from this alkaline solution, the extract was made up to 100 ml., and the optical density was measured at a wavelength characteristic of the ester (*ca.* 260 mμ) with a Unicam SP 500. The extraction technique, although tedious and lengthy, was found to give good Beers law plots for methyl 4-nitrobenzoate and isopropyl benzoate. A blank experiment, with only 4-nitrobenzoic acid in the sodium hydrogen carbonate solution, showed no change in the u.v. spectrum of the ether after two extractions.

The reaction was established to be a hydrolysis by analysis of the sodium hydrogen carbonate layer. This was found to contain quantitative amounts of the corresponding benzoic acid in the hydrolysis of methyl 4-nitrobenzoate and isopropyl benzoate.

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