313. *Organic Reactions in Sulphuric Acid. Part I. Ester Hydrolysis.*

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It is shown that, in the hydrolysis by sulphuric acid of methyl, ethyl, and *iso*propyl benzoate, the change of mechanism which occurs between the ethyl and the *iso*propyl ester[1] is from $A_{AC}1$ to $A_{AL}1$. A cryoscopic method is described for measuring rates of reactions in sulphuric acid solutions.

The rate of hydrolysis of alkyl benzoates has been shown to vary as follows: methyl > ethyl < *iso*propyl < *tert.*-butyl.[1] The fact that the rate passes through a minimum suggests that a change of mechanism occurs in the middle of the series. This change of mechanism has been variously interpreted,[2] but on the basis of very little experimental evidence. In the present work evidence has been obtained by studying the hydrolysis of esters under varied experimental conditions, and in particular by finding the effect of polar substitution on the rate.

(1) *Evidence for the Unimolecular Hydrolysis of Methyl Benzoate.*—Graham and Hughes[3] found that the hydrolysis of methyl benzoate is of zero order with respect to water in 98—99·9% aqueous sulphuric acid. They concluded that the reaction is unimolecular. Newman, Craig, and Garrett[2b] have suggested, however, that the reaction is bimolecular, proceeding through an attack on the conjugate acid of the ester by the bisulphate ion.

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[1] Kuhn, *J. Amer. Chem. Soc.*, 1949, **71**, 1575.

[2] (*a*) Ref. 1; (*b*) Newman, Craig, and Garrett, *ibid.*, p. 869; (*c*) Gillespie and Leisten, *Quart. Reviews*, 1954, **8**, 40.

[3] Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons Ltd., London, 1953, p. 771.

The rate of the hydrolysis has been measured cryoscopically in aqueous and in 100% sulphuric acid, and in dilute oleum. Expts. 1—3 (Table 1) show that the first-order rate constant is almost independent of the initial concentration of the ester, and therefore of the bisulphate ion, since methyl benzoate ionises as a strong base in sulphuric acid, according to equation (1):[2b]

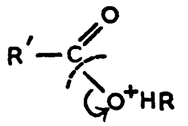
$$\mathrm{Ph{\cdot}CO_2Me + H_2SO_4 = Ph{\cdot}CO_2MeH^+ + HSO_4^-} \quad . \; . \; . \; . \; . \; . \; . \quad (1)$$

These results therefore eliminate the possibility of a rate-determining attack by the bisulphate ion. (A large increase in the concentration of ester reduces the rate, presumably through its effect on the medium. Thus the rate constant at 20°, calculated from these results, is 15% higher than that found by Graham and Hughes,[4] who used a concentration of ester approximately five times greater than that in the present work.) The rates are similar in 100% and in aqueous sulphuric acid; the rate is actually greater in oleum (Expts. 2, 4, and 6), emphatically confirming that water is not involved in the rate-determining step.

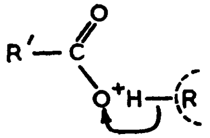
The present work thus supports the conclusion that the hydrolysis of methyl benzoate in sulphuric acid is unimolecular.

(2) *Polar Effects on Ester Hydrolysis in Sulphuric Acid.*—The effect of polar substituents on the rate of hydrolysis of esters has been predicted by Day and Ingold.[5] For acid-catalysed unimolecular hydrolysis it is necessary to estimate the effect both on the position of the equilibrium $\mathrm{R'{\cdot}CO_2R + HA \rightleftharpoons R'{\cdot}CO_2RH^+ + A^-}$ and on the heterolysis of the conjugate acid of the ester. For most esters in sulphuric acid, however, this equilibrium lies far to the right-hand side,[2c] and so the influence of substitution must be confined to the heterolysis stage. For this reason, in sulphuric acid and all media of similar or greater acidity, substitutive effects should differ considerably from those predicted by Day and Ingold both for acyl–oxygen fission (the $A_{\mathrm{AC}}1$ mechanism) and for alkyl–oxygen fission (the $A_{\mathrm{AL}}1$ mechanism):

($A_{\mathrm{AC}}1$)



($A_{\mathrm{AL}}1$)



Electron-donating substituents in R′ should aid, and in R retard, $A_{\mathrm{AC}}1$ heterolysis but have the opposite effects on $A_{\mathrm{AL}}1$ heterolysis. Electron-attracting substituents in R′ should retard, and in R aid, $A_{\mathrm{AC}}1$ heterolysis but again have contrary effects in the $A_{\mathrm{AL}}1$ case.

The influence on the rate of hydrolysis of methyl benzoate of each of these four types of substitution is known. Graham and Hughes[3] found the rate of hydrolysis of methyl *p*-toluate to be four times that of methyl benzoate, and concluded that the mechanism is $A_{\mathrm{AC}}1$. This conclusion follows equally from Day and Ingold's discussion of substitutive effects and from the present one. Qualitative comparisons of rate have been made for a large number of esters by Kuhn and Corwin,[6] and, recently, by Bradley and Hill,[7] with no clear interpretation of the results. In fact, all these results * show the effects predicted above for the $A_{\mathrm{AC}}1$ mechanism, thereby substantiating the present approach to polar effects on ester hydrolysis in sulphuric acid, as well as providing evidence for the mechanism of hydrolysis of methyl benzoate.

The effect of polar substitution on the hydrolysis of ethyl and *iso*propyl benzoate has been determined previously in only one case: Kuhn[1] compared qualitatively the rates of hydrolysis of these esters and their *p*-methoxy-derivatives. It was later shown that such derivatives are sulphonated rather rapidly in sulphuric acid,[8] and since, in addition, the polar effect of the free methoxy-group is the reverse of that of the protonated group, conclusions cannot be drawn from these results.

* See also Table 2, in which the rates of hydrolysis of methyl benzoate, methyl *p*-nitrobenzoate, and ethyl benzoate are compared at 65°.

[4] Personal communication; cf. Graham, Thesis, London, 1943.

[5] Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686.

[6] Kuhn and Corwin, *J. Amer. Chem. Soc.*, 1948, **70**, 3370.

[7] Bradley and Hill, *ibid.*, 1955, **77**, 1575.

[8] Newman and Deno, *ibid.*, 1951, **73**, 3651.

The rates of hydrolysis of ethyl benzoate and its *p*-nitro-derivative have been determined cryoscopically. The rate constant for ethyl *p*-nitrobenzoate and an extrapolated value for ethyl benzoate are compared at 65° in Table 2. The rates of hydrolysis of *iso*propyl benzoate and *p*-nitrobenzoate have been measured under identical conditions, in this case semiquantitatively (Table 2). Whereas the introduction of the *p*-nitro-group into ethyl benzoate leads to a sixty-fold *decrease* in rate, yet in the case of *iso*propyl benzoate it leads to a two hundred-fold *increase*. The size of the effects is evidence that the reactions are not bimolecular:[5] the directions of the effects provide evidence for acyl–oxygen fission in the case of ethyl benzoate, and for alkyl–oxygen fission in the case of *iso*propyl benzoate. *tert.*-Butyl benzoate should have a greater tendency to alkyl–oxygen fission than *iso*propyl benzoate: accordingly, it has the greater rate of hydrolysis in sulphuric acid.[1] Moreover, *tert.*-butyl esters have been shown to be hydrolysed by the $A_{AL}1$ mechanism in other solvents.[9] Thus the change of mechanism in the hydrolysis of this series of esters is from $A_{AC}1$ in the case of methyl and ethyl benzoate, to $A_{AL}1$ in the cases of *iso*propyl and *tert.*-butyl benzoate.

FIG. 1. *The change of* i*-factor with time in the hydrolysis of methyl benzoate.*

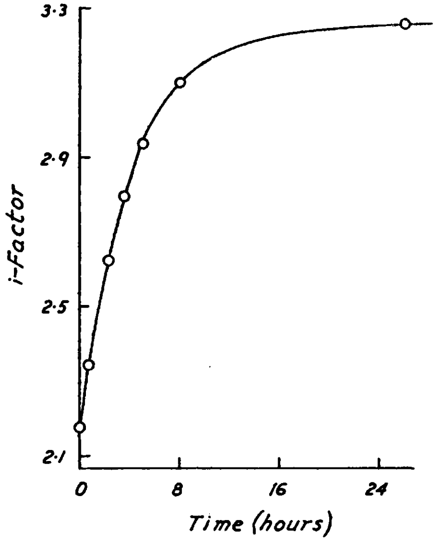
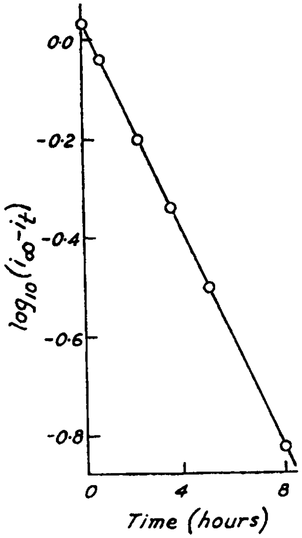


FIG. 2. *The cryoscopic determination of the rate constant.*



Both graphs relate to Expt. 3 (Tables 1 and 3).

It is reasonable to suppose that suitable substitution in ethyl or *iso*propyl benzoate might lead to changes in the mechanism of hydrolysis. It is possibly significant in this connection that, whereas hydrolysis of methyl benzoate is faster than that of ethyl benzoate, the reverse is true of the *p*-nitro-derivatives.

(3) *Instability of the Benzoyl Ion in Sulphuric Acid.*—The $A_{AC}1$ mechanism for the hydrolysis of methyl benzoate requires that the rate-determining step should be

$$\mathrm{Ph{\cdot}CO_2MeH^+ = Ph{\cdot}CO^+ + MeOH}$$

The question arises whether the benzoyl ion remains as such, or whether it extracts water from the solvent to form the benzoic acidium ion, *i.e.*, whether the overall reaction is correctly represented by equation (2) or by equation (3):

$$\mathrm{Ph{\cdot}CO_2Me + 3H_2SO_4 = Ph{\cdot}CO^+ + H_3O^+ + 2HSO_4^- + MeHSO_4} \quad . \quad . \quad . \quad . \quad (2)$$

$$\mathrm{Ph{\cdot}CO_2Me + 2H_2SO_4 = Ph{\cdot}CO_2H_2^+ + HSO_4^- + MeHSO_4} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

A previous experiment to determine this led to an equivocal result.[2b]

[9] Bunton and Wood, *J.*, 1955, 1522; Stimson, *J.*, 1955, 2010, 2673.

Fig. 1 shows the change of the *i*-factor with time at constant temperature of methyl benzoate in sulphuric acid, in a typical experiment. The *i*-factor approaches a limiting value of approximately 3, and analysis of the solution shows that at this stage hydrolysis is complete (see Table 3). These results together show that the overall reaction is according to equation (3). The fact that the cryoscopic method yields a rate constant when the solvent is oleum confirms this conclusion, for a reason that is explained below (p. 1576).

This evidence for the instability of the benzoyl ion is similar in type to that provided by a recent study of the behaviour of benzoic anhydride in sulphuric acid,[10] but is perhaps more convincing in that the formation of the benzoyl ion as a reaction intermediate has been better demonstrated in the present case.

RESULTS

TABLE 1. *The rate of hydrolysis of methyl benzoate in sulphuric acid and oleum.*

	Molality					Molality			
Expt.	H_2O	Ester	Temp.	k_1 (hr.$^{-1}$)	Expt.	H_2O	Ester	Temp.	k_1 (hr.$^{-1}$)
1	0·068	0·0231	25·1°	0·255	—	0·078	0·485	20·0°	0·095 *
2	0·069	0·0869	25·1	0·250	2, 5	0·068—	0·0869—	20·0	0·111 †
3	0·065	0·1830	25·1	0·247		0·069	0·0902		
4	0·00	0·0927	25·1	0·255		SO_3	Ester		
5	0·068	0·0902	34·55	1·046	6	0·074	0·0513	25·1	0·357

* This result was obtained by Graham and Hughes.[4]

† Calculated from the results of Expts. 2 and 5, Arrhenius temperature dependence being assumed.

TABLE 2. *The rate of hydrolysis of esters in aqueous sulphuric acid.*

		Molality			
Expt.	Ester	H_2O	Ester	Temp.	k_1 (hr.$^{-1}$)
7	Ethyl benzoate	0·071	0·0848	25·1°	0·0854
8	Ethyl benzoate	0·067	0·0794	34·55	0·403
2, 5	Methyl benzoate	0·068—0·069	0·0869—0·0902	64·0	52·4
9	Methyl *p*-nitrobenzoate	0·066	0·0863	64·0	0·277
7, 8	Ethyl benzoate	0·067—0·071	0·0794—0·0848	64·0	29·0
10	Ethyl *p*-nitrobenzoate	0·066	0·0807	64·0	0·456
11	*iso*Propyl benzoate	0·068	0·23	9	0·6 *
12	*iso*Propyl *p*-nitrobenzoate	0·068	0·23	9	120 *

* Approximate values.

TABLE 3. *Summarised cryoscopic results.**

Expt.	Initial *i*-factor	Time (hr.)	Final *i*-factor	i_∞	Expt.	Initial *i*-factor	Time (hr.)	Final *i*-factor	i_∞
1	1·93	21·2	3·01	2·99	6	0·79	22·4	1·81	1·80
2	2·02	—	—	3·06	7	2·04	—	—	3·08
3	2·17	26·0	3·26	3·25 †	8	2·03	20·0	3·07	3·05
4	2·06 ‡	27·2	3·13	3·10	9	1·77	28·8	2·88	2·86
5	2·03	7·7	3·07	3·04	10	1·91	17·8	3·45	3·00 §

* The "Final *i*-factors" in col. 4 are experimentally determined infinity values recorded after periods of reaction given in col. 3. The values of i_∞ (col. 5) are those which lead to the best first-order plots. Other information concerning these experiments is in Tables 1 and 2.

† 98·7% (± 2%) of the theoretical yield of benzoic acid was found by analysis of the solution at the end of this run.

‡ A hypothetical value (10·43°) of the freezing point of the solvent was chosen to give an initial *i*-factor consistent with those found in aqueous sulphuric acid.

§ This value was chosen by reference to Expt. 9, and the rate constant was determined from the earlier freezing-point measurements. Ethyl hydrogen sulphate is clearly somewhat unstable in sulphuric acid at 65°.

EXPERIMENTAL

Materials.—Commercial samples of methyl, ethyl, and *iso*propyl benzoate were distilled *in vacuo* : the fractions used boiled over a 1° range. Methyl *p*-nitrobenzoate (m. p. 95—95·5°), ethyl *p*-nitrobenzoate (m. p. 56°), and *iso*propyl *p*-nitrobenzoate (m. p. 105—106°) were purified by washing ethereal solutions with aqueous alkali and recrystallising the solids from ethanol.

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[10] Leisten, *J.*, 1955, p. 298.

Determination of Reaction Rates from Freezing-point Measurements.—Cryoscopic determination of reaction rates in sulphuric acid depends upon the fact that the freezing point of a sulphuric acid solution varies in an almost linear way with the number of solute particles in the solution. The method is widely applicable to the study of reactions in sulphuric acid,[11] and will be illustrated by reference to the hydrolysis of methyl benzoate. The rate constants in Table 1 were obtained by plotting the logarithm of $(i_\infty - i_t)$ against time, where i_∞ is the i-factor corresponding to complete reaction and i_t the i-factor after the solution has been at the reaction temperature for a time t. Fig. 2 is a typical plot. It is seen by reference to equations (1) and (3) that in the course of the reaction the conjugate acid of the ester is replaced by that of benzoic acid, a process which should not lead to appreciable change of freezing point: at the same time a molecule of the non-electrolyte methyl hydrogen sulphate is produced. Thus from the beginning to the end of the hydrolysis the i-factor should increase by $1{\cdot}0 \pm 0{\cdot}1$, the uncertainty arising from the fact that the number of particles per solute molecule may differ from the i-factor by as much as 10%. In the present work the value of i_∞ chosen to give the best first-order plot varied from 1·01 to 1·08 above that of the initial i-factor. The experimental value of i_∞ (recorded after approximately ten times the half-life of the reaction) varied from 1·02 to 1·09 above the initial i-factor. The fact that the optimum values of i_∞ are close both to the experimental values and to those predicted from the stoicheiometry of the reaction shows that for suitable reactions the method is sound. In a typical case (Expt. 4) the use of a value of i_∞ 0·01 above the optimum led to a rate constant only 1·3% lower than that recorded. The method is simple to operate, avoids analytical difficulties, and requires only small concentrations of solute. There are a number of limitations. The reaction must be negligibly slow in the temperature region in which the freezing-point measurements are made (5—10°), and must lead to stable products: *e.g.*, *iso*propyl esters cannot be studied in this way since the *iso*propyl hydrogen sulphate formed undergoes further slow reactions.[12] It is of course necessary that the reactions be accompanied by a change in the number of solute particles: when the solvent is oleum, this change must be in the number of solute *molecules*, and the number of *ions* must remain the same, because in oleum only non-electrolytes produce a nearly linear depression of the freezing point.[13] We have already seen that hydrolysis according to equation (3) satisfies this last condition, and should therefore expect to observe first-order kinetics in the hydrolysis of methyl benzoate in oleum when studied by the cryoscopic method: that this is in fact found is a further verification of equation (3).

The cryoscopic technique and the method of computing i-factors have been previously described.[14] After the initial freezing-point determination the solution was heated rapidly to the reaction temperature by placing the cryoscope in a water-bath at 10° above this temperature. The cryoscope was then transferred to a thermostat. After the required interval of time the solution was rapidly chilled and the freezing point re-determined. For the runs at 65°, the thermometer was replaced by a ground-glass stopper between measurements: the thermometer was rinsed, dried with filter-paper, and stored over anhydrous magnesium perchlorate.

Estimation of Benzoic Acid in Sulphuric Acid.—20 ml. (36·71 g.) of the crysocopic solution (from Expt. 3) were pipetted on to 35 g. of ice in a 100 ml. tall-form beaker immersed in a freezing mixture. The liquid was removed with a filter stick, and the wet precipitate of benzoic acid transferred to a 500 ml. wide-necked flask with hot water. Excess of barium chloride was added to replace the sulphuric acid in the mixture by hydrochloric acid, and the volume was made up to 200 ml. with distilled water. The solution was titrated conductometrically with 0·5N-ammonia. The weight of benzoic acid thus found was 0·768 g. The solubility loss was estimated [15] at 0·022 g. This correction being applied, the weight found was 0·790 g., corresponding to 98·7% hydrolysis. The uncertainty of this result is mainly that of the solubility correction. It was found that this estimation cannot be performed gravimetrically, because in freeing the precipitate from sulphuric acid considerable loss of benzoic acid occurs. The mixture of benzoic acid and sulphuric acid cannot be titrated directly because the sulphuric acid branch of the neutralisation curve is not linear, probably on account of the rather weak second dissociation of sulphuric acid.

Semiquantitative Rate Measurements.—2 ml. of sulphuric acid at 9° were added to each tube

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[11] Leisten, unpublished experiments.

[12] Oddo and Scandola, *Gazzetta*, 1909, **39**, 1.

[13] Gillespie, *J.*, 1950, 2516.

[14] Gillespie and Leisten, *J.*, 1954, 1.

[15] Hammett and Chapman, *J. Amer. Chem. Soc.*, 1934, **56**, 1282; "Handbook of Chemistry and Physics," Chemical Rubber Publ. Co., Cleveland, Ohio, 1948, p. 666.

containing the required amount of ester, the tube being immersed in a thermostat at 9°. The ester was dissolved by stirring. The tube was withdrawn after the required interval of time and the contents were poured on an equal weight of ice cooled by solid carbon dioxide. The mixture was filtered. In the case of *iso*propyl benzoate the size of the benzoic acid precipitate on the filter paper was compared visually for different times of reaction :

Time of reaction (min.)	15	30	70	∞
Relative size of ppt.	1	2	4	8
Estimated half-life	70 min.			

In the case of *iso*propyl *p*-nitrobenzoate, the precipitate obtained by pouring the reaction mixture on ice was treated with alkali to separate the ester from the acid. The acid was then re-precipitated by acidification. The amounts of both ester and acid were compared visually : by this means the half-life was estimated to be 20 sec.

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