186. *Tracer Studies in Ester Hydrolysis. Part IV.* The Hydrolysis of Diphenylmethyl Formate and Acetate.*

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In hydrolysis of diphenylmethyl formate under acidic and basic conditions the acyl–oxygen bond is broken, but in an initially neutral solution alkyl–oxygen fission occurs. The latter result is supported by the observation of carbonium-ion capture by the thiocyanate ion in initially neutral solution. Acyl–oxygen bond fission is found for the acid hydrolysis of diphenylmethyl acetate.

MECHANISTIC studies of hydrolysis of carboxylic esters show that substitution by electron-releasing groups on the α-alkyl-carbon atom increases the ease of fission of the alkyl–oxygen bond.[1] In particular there is a parallelism between the S_N1 reactivity of an alkyl halide and the ease of alkyl–oxygen bond fission in the corresponding carboxylic ester. For example, Kenyon and his co-workers provided numerous instances of alkyl–oxygen bond fission in reactions of the hydrogen phthalates of secondary alcohols containing electron-releasing groups,[2] and this bond fission is found in the acid hydrolyses of *tert.*-butyl[3] and ethyldimethylpentyl acetates,[4] and in the acid, neutral, and basic hydrolyses of triphenylmethyl acetate.[5] It might be expected therefore that esters of diphenylmethanol would provide suitable systems for the observation of hydrolyses with alkyl–oxygen bond fission. Hydrolysis of the formate was examined under a variety of

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* Part III, *J.*, 1956, 1079.

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

[2] Davies and Kenyon, *Quart. Rev.*, 1955, **9**, 203.

[3] Bunton and Wood, *J.*, 1955, 1522.

[4] Bunton, Hughes, Ingold, and Meigh, *Nature*, 1950, **161**, 680.

[5] Bunton and Konasiewicz, *J.*, 1955, 1354.

conditions (the results of the rate studies are tabulated). In accordance with observations on other alkyl formates [6] the attack of hydroxide ion (with acyl–oxygen bond fission) was very rapid. The acid hydrolysis is considerably slower than the alkaline hydrolysis, and it too involves acyl–oxygen bond fission. Rate comparisons with acid-catalysed hydrolyses of other non-sterically hindered esters [7] suggest a bimolecular rather than a unimolecular mechanism. The rate dependence on temperature follows the equation: $k_A = 1{\cdot}41 \times 10^{-8} \exp(-16{,}100/\boldsymbol{R}T)$. These values for the Arrhenius parameters are similar to those observed in other hydrolyses by mechanism $A_{Ac}2$ (see, *e.g.*, ref. 8). Similarly the ratio of the second-order rate coefficients for the acid and the basic hydrolysis is of the same order of magnitude as observed in bimolecular ester hydrolyses with acyl–oxygen bond fission.[7]

TABLE 1. *Rates of hydrolysis in aqueous dioxan.*

Solvent: aqueous 70% dioxan (except where otherwise specified).

(*A*) Diphenylmethyl formate at 35° (except where otherwise specified).

[HCl] (M)	0·0246	0·0491	0·0986	0·0986	0·0536	0·111
$10^6 k_1$ (sec.$^{-1}$)	10·6, 10·3	20·3, 20·6	42·9, 44·3	1·45,* 1·54 *	73·2 †	169 †

k_A (at 0°) = $1{\cdot}52 \times 10^{-5}$; k_A (at 35°) = $45{\cdot}5 \times 10^{-5}$ sec.$^{-1}$ mole^{-1} l.

* Temp. 0°. † Solvent: aq. 75% dioxan; temp. 50°

(*B*) Effect of added reagents; [HCl] = 0·0986M.

Reagent	H·CO$_2$H	NaCNS	NaClO$_4$		
[Reagent] (M)	0·115	0·0367	0·021	0·126	0·171
$10^6 k_1$ (sec.$^{-1}$)	45·5	43·1	44·8	50·9	56·3

(*C*) Base hydrolysis; [Ba(OH)$_2$] = 0·005M; [Ester] = 0·008M.

Temp. 0°. k_2 = 0·430, 0·425 sec.$^{-1}$ mole^{-1} l. (independent expts.).

D) Initially neutral hydrolysis; temp. 99·2°; initial $k_1 = 6{\cdot}10 \times 10^{-6}$ sec.$^{-1}$.

Diphenylmethyl acetate. Temp. 99·5°.

[HCl] (M)	0·020	0·030	0·040	0·060
$10^4 k_1$ (sec.$^{-1}$)	1·79	2·40	3·40	5·07

$k_A = 8{\cdot}3 \times 10^{-4}$ sec.$^{-1}$ mole^{-1} l.

Hydrolysis of diphenylmethyl acetate was followed under acid conditions only. It was slower than that of the formate, and by extrapolation of the formate rate values to the temperature of the acetate runs we calculate that the formate is hydrolysed in acid *ca.* 55 times faster than the acetate. Determination of the position of bond fission in the acid hydrolysis of the acetate, by using ^{18}O as tracer, was complicated by the acid-catalysed oxygen exchange between water and diphenylmethanol. Since acetic acid undergoes exchange so rapidly under the experimental conditions it was pointless to study its abundance. The isotopic abundances of the diphenylmethanol isolated from control tests and from the acid hydrolyses are, however, consistent with hydrolysis by acyl–oxygen bond fission. Both esters therefore react by the same mechanism in acid solution.

Hydrolysis of the formate in initially neutral solution was much slower than in the presence of acid or alkali. The formic acid produced catalysed the hydrolysis, and the first-order rate coefficient quoted in Table 1 is therefore calculated from the initial rate. Tracer studies with diphenylmethanol isolated from hydrolysis in initially neutral solution showed that its oxygen was in part derived from the solvent, and control tests proved that exchange between alcohol and solvent could not account for this isotopic enrichment. There was therefore at least some alkyl–oxygen fission in the neutral hydrolysis. The exact amount could not be determined readily, partly because of the exchange already

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[6] Humphreys and Hammett, *J. Amer. Chem. Soc.*, 1956, **78**, 521.

[7] Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1939, pp. 212—213.

[8] Drushel, *Annalen*, 1915, **39**, 113; **40**, 643; Skrabal and *et al.*, *Monatsh.*, 1926, **47**, 17, and later papers.

mentioned, but also because those ester molecules whose hydrolysis is catalysed by formic acid will undergo acyl–oxygen fission, and their number will increase as the reaction proceeds.

TABLE 2. *Position of bond fission.*

(1) *Diphenylmethyl formate.*

(i) Solvent: aqueous 70% dioxan. Temp. 35·0°. Isotopic abundance of water = 0·550 atom % excess. (Method A.)

	[HCl] (M)	Abundance of product (atom % excess)	Oxygen (%) derived from water
Hydrolysis:	0·0784	0·034	6
	0·141	0·042	7
Control:	0·0996	0·040	8

(ii) Solvent: aqueous 75% dioxan. Temp. 50°. Isotope measurements determined by density, relative to London tap water.

[HCl] (M)	Density of water (p.p.m.)	Density of water from product (p.p.m.)	Oxygen (%) derived from water
0·203	+293	+13, +4	4·4, 1·3
0·200	+298	+5	1·7

Control tests under the experimental conditions gave samples of diphenylmethanol which gave water of relative densities +20, +7 p.p.m.

(iii) Basic hydrolysis. Solvent: aqueous 70% dioxan. [NaOH] = 0·1M. Temp. 0°. Isotopic abundance of water = 0·727 atom % excess. Abundance of product = 0·008 atom % excess. (Method B.)

(iv) Initially neutral. Solvent: aqueous 70% dioxan. Temp. 99·5°. [Ester] = *ca.* M/7. Isotopic abundance of water = 0·476 atom % excess. (Method B.)

	Time (hr.)	Abundance of product (atom % excess)	Oxygen (%) derived from water
Hydrolysis:	54	0·270	57
	32	0·233	49
Control:	42 [a]	0·140	29
	30 [b]	0·042	8·8

H·CO$_2$H: (*a*) 0·2M, (*b*) 0·1M.

(2) *Diphenylmethyl acetate.*

Solvent: aqueous 70% dioxan. Temp. 99·5°. Isotopic abundance of water = 0·483 atom % excess. (Method B.)

	[HCl] (M)	Time (hr.)	Abundance of product (atom % excess)	Oxygen (%) from water
Hydrolysis:	0·06	3	0·294	61
	0·12	1·5	0·366	76
Control:	0·06	1·7	0·283	59
	0·12	0·8	0·390	81

In confirmation of these postulated mechanisms, we find that the thiocyanate ion intervenes in the neutral, but not in the acid, hydrolysis. This reagent forms a stable product with the diphenylmethyl cation, and so a method is available for the detection of this ion. In the hydrolysis of diphenylmethyl chloride in aqueous 70% dioxan, at 35°, almost half the carbonium ions produced are captured by the thiocyanate ion. Under initially neutral conditions, in the same solvent at 99·5°, *ca.* 20% of the total reaction is diverted to alkyl thiocyanate or *iso*thiocyanate.

EXPERIMENTAL

Materials.—Diphenylmethyl formate was first prepared by Bacon [9] by interaction of diphenylmethyl chloride and sodium formate in formic acid. This method was used for some samples; it was necessary to use carefully dried materials. After 3 days' heating on a steam-bath the product was extracted with light petroleum, volatile materials were pumped off, and after distillation (b. p. 104°/0·4 mm.) the ester slowly crystallised, having m. p. 22° (Found: C, 79·0; H, 5·9. Calc. for $C_{14}H_{12}O_2$: C, 79·2; H, 5·7%).

Later samples of the ester were prepared more simply by reaction of diphenylmethanol with acetic formic anhydride containing a trace of sodium formate. Acetic acid and excess of

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[9] Bacon, *Amer. Chem. J.*, 1905, **33**, 88.

anhydride were pumped off. The ester crystallised. A third method was used with partial success: diphenylmethanol was heated with sodium formate in dry formic acid saturated with hydrogen bromide; ester prepared by this method did not solidify and probably contained diphenylmethanol and possibly bisdiphenylmethyl ether.

Diphenylmethyl acetate was prepared by heating acetic anhydride containing diphenylmethanol under reflux for 3 hr. The solvent was pumped off; the ester purified by crystallisation from light petroleum had m. p. 41°.

Kinetic Runs.—Reactions were carried out in aqueous dioxan which, in general, contained 70% by volume of purified dioxan. The kinetics were followed by acid–base titration; in experiments on the formate it was essential to avoid building up of local concentrations of alkali during titration, because of the high rate of basic hydrolysis.

Both thiocyanate ion and picric acid were tried as intervening agents. Tests on the hydrolysis of diphenylmethyl chloride at 35°, in aqueous 70% dioxan containing hydrochloric acid, showed that 44% of the total reaction product was alkyl thiocyanate or *iso*thiocyanate. Thiocyanate ion did not intervene in the acid hydrolysis, and its small effect on the rate (Table 1) was due to its ionic strength effect; this ion did, however, intervene effectively in the neutral hydrolysis of diphenylmethyl formate at 99°. Picric acid did not intervene in the hydrolysis of diphenylmethyl chloride under the conditions of the acid hydrolysis of diphenylmethyl formate; its use was not investigated further.

Position of Bond Fission.—Tracer experiments were made with the solvent water enriched in ^{18}O. In the early work the isotopic abundance was determined by density measurements; mass-spectrometric assay was used for later samples.

Diphenylmethanol, isolated from hydrolysis under kinetically controlled conditions, was purified by recrystallisation from light petroleum and dried in a vacuum-desiccator. The isotopic abundances of the isolated samples were determined by various methods. (i) *Ca.* 4 g. were cracked over platinised quartz at 1100° in a stream of dried, oxygen-free hydrogen, and the oxides of carbon so formed were then reduced to water over thoriated nickel. The general conditions were those described by Russell and Fulton.[10] The isotopic abundance of this water was determined by density measurements, by procedures already described,[11] or after electrolysis of a small part in a divided cell, by mass-spectrometric assay (method A). (ii) The alcohol was pyrolysed to carbon monoxide *in vacuo* in a carbon tube heated in an R.F. induction furnace. The carbon monoxide was analysed mass spectrometrically (method B). To minimise errors due to dilution and isotopic fractionation similar methods of analysis were used for the water and the diphenylmethanol.

DISCUSSION

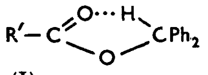
Hydrolysis of diphenylmethyl formate in alkaline solution by mechanism $B_{Ac}2$ is very rapid, as might be expected from consideration of the known properties of formate esters.[6] This high reactivity is not found in acid hydrolysis, and similarly diphenylmethyl acetate is less reactive than its aliphatic counterpart.[12] This comparatively low reactivity in acid solution is therefore common to both formate and acetate. The facility of the alkaline hydrolysis, together with inspection of molecular models, suggests that steric hindrance at the acyl(carbonyl)-carbon atom is of minor importance, and tracer studies show that in both alkaline and acid solution the reagent attacks this atom. The results in acid solutions were somewhat unexpected because alkyl–oxygen bond fission is observed in the acid hydrolyses of the acetates of triphenylmethanol[5] and tertiary aliphatic alcohols,[3,4] compounds which give respectively more and less stable carbonium ions than are derived from a diphenylmethyl compound.

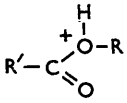
This comparatively low reactivity in acid solution of both the formate and acetate of diphenylmethanol is probably due to the lowering of the basicity of these esters by substitution of two phenyl groups on the alkyl-carbon atom.

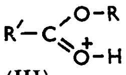
Hydrogen bonding,[13] as in (I), would reduce the basicity of the ester molecule and

[10] Russell and Fulton, *Ind. Eng. Chem., Anal.*, 1933, **5**, 384.
[11] Datta, Day, and Ingold, *J.*, 1939, 838.
[12] Bell, Dowding, and Noble, *J.*, 1955, 3106.
[13] Curran, *J. Amer. Chem. Soc.*, 1945, **67**, 1835.

might also facilitate acyl–oxygen bond fission in the neutral and basic hydrolyses. The $-I$ effect of the phenyl groups, while reducing the basicity of the ester, would facilitate this hydrogen bonding. These effects will reduce the standing concentration of the conjugate acid of the ester and hence the overall rate of reaction. This factor alone does not explain the apparently anomalous position of bond fission in the acid hydrolysis. Protonation of a carboxylic ester may occur on either the ethereal or the carbonyl-oxygen atom, giving conjugate acid (II) and (III). The relative amounts of these acids will depend on the relative basicities of the two oxygen atoms, and either of them may in principle be the reactive species in any acid hydrolysis. There is considerable evidence that acid-catalysed alkyl–oxygen bond fission gives a carbonium ion, by a reaction which should occur more readily in structure (II), where the positive charge is largely on the atom adjacent to the breaking bond. Acid hydrolysis with acyl–oxygen bond fission requires addition of a water molecule to the acyl(carbonyl)-carbon atom,[14] except in certain special systems where a unimolecular mechanism can be observed.[1, 15] This addition should be facilitated by protonation of the acyl-oxygen atom, as in structure (III). We might therefore expect the relative ease of acyl– or alkyl–oxygen bond fission to be governed, not only by the tendency of the alkyl group to form a carbonium ion, but also by the position of protonation. Substitution of two phenyl groups on the α-alkyl-carbon atom will reduce the basicity of both the oxygen atoms in an ester molecule, hence tending to reduce the rate of acid hydroysis, but the effect will be greater on the nearer, ethereal oxygen atom. Structure (III) will therefore be favoured over structure (II), and hence attack of water molecules on the acyl-carbon atom, with consequent acyl–oxygen bond fission, will be preferred, despite the high stability of the diphenylmethyl carbonium ion.[16]


(I)


(II)


(III)

These considerations do not apply to hydrolysis in neutral solution (though our experimental observations are complicated by autocatalysis by formic acid). Here the mechanism should be governed solely by the relative ease of heterolysis of the alkyl–oxygen bond, and of bimolecular attack on the acyl-carbon atom. Tracer experiments prove the existence of some alkyl–oxygen bond fission, although the complications of autocatalysis of both hydrolysis and subsequent oxygen exchange between the alcohol and water prevent our determining its exact extent. Further, in initially neutral solution, diphenylmethyl formate is hydrolysed more rapidly than are *tert.*-butyl carboxylates,[17] but less rapidly than is triphenylmethyl acetate.[5] This rate sequence for neutral hydrolysis is that predicted from the relative ease of formation of the carbonium ions. The intervention of thiocyanate ion in neutral, but not in acid, hydrolysis supports the mechanisms which we propose.

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[14] Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626.
[15] Long and Purchase, *ibid.*, 1950, **72**, 3267.
[16] Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603.
[17] Bunton, Comyns, Graham, and Quayle, *J.*, 1955, 3817.