698. *The Kinetics of Alkyl–Oxygen Fission in Ester Hydrolysis. Part V.* Diphenylmethyl Esters in Aqueous Acetone.*

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The kinetics of the acid-catalysed hydrolysis of diphenylmethyl 2 : 4 : 6-trimethylbenzoate, benzoate, acetate, and formate have been studied. The activation energy is *ca.* 30 kcal./mole for the 2 : 4 : 6-trimethylbenzoate and benzoate, for which mechanism $A_{AL}1$ is suggested, and 18 kcal./mole for the formate, in accordance with mechanism $A_{AC}2$. The Arrhenius equation is not followed in the case of the acetate and hydrolysis by the two mechanisms simultaneously is suggested.

THE kinetics of acid-catalysed hydrolyses of *tert.*-butyl esters of acids with varying ability to facilitate $A_{AC}2$ hydrolysis, *viz.*, 2 : 4 : 6-trimethylbenzoic, benzoic, acetic, and formic, have been studied.[1] It has been suggested that the activation energy for $A_{AL}1$ hydrolysis is *ca.* 30 kcal./mole and that a transition in mechanism occurs with the acetate, for which, however, the mechanism of hydrolysis is predominantly $A_{AL}1$. This has been established by Bunton and Wood [2] by the use of [18]O. Further evidence in support of the suggestion that alkyl–oxygen fission in acid-catalysed hydrolysis is accompanied by an activation energy of *ca.* 30 kcal./mole is available. Bunton, Comyns, Graham, and Quayle [3] find E to be 29·3 kcal./mole for the acid-catalysed hydrolysis of *tert.*-butyl 2 : 4 : 6-triphenyl-benzoate, and Dostrovsky and Klein [4] give the value of 30 kcal./mole for the acid-catalysed oxygen exchange of *tert.*-butyl alcohol. In S_N reactions diphenylmethyl shows electron-releasing power comparable with that of *tert.*-butyl, so that its esters should have a similar tendency to $A_{AL}1$ hydrolysis. The formate, however, is known to undergo acyl–oxygen fission.[5] The kinetics of hydrolysis of diphenylmethyl 2 : 4 : 6-trimethylbenzoate, benzoate, acetate, and formate are now reported.

EXPERIMENTAL

Materials.—Diphenylmethanol (15 g.) and 2 : 4 : 6-trimethylbenzoic acid (25 g.) were heated gently during 11 hr. while water escaped. The residue was dissolved in ether, washed with 10% aqueous sodium hydroxide (8 g. of 2 : 4 : 6-trimethylbenzoic acid being recovered), and dried, and the ether evaporated. The crude *diphenylmethyl 2 : 4 : 6-trimethylbenzoate* (17 g.) was recrystallised from methanol to constant m. p. (90·5°) (9 g.) (Found : C, 83·7; H, 6·9. $C_{23}H_{22}O_2$ requires C, 83·6; H, 6·7%).

Diphenylmethyl benzoate (crude yield 16 g.), prepared from diphenylmethanol (20 g.), benzoyl chloride (10 ml.), and pyridine (5 ml.), was recrystallised from methanol to constant m. p. (91·5°) (Found : C, 83·4; H, 5·5. Calc. for $C_{20}H_{16}O_2$: C, 83·3; H, 5·6%).

Diphenylmethyl acetate (m. p. 42°) was prepared from diphenylmethanol and acetic anhydride (Found : C, 79·7; H, 6·4. Calc. for $C_{15}H_{14}O_2$: C, 79·6; H, 6·2%).

Diphenylmethyl formate (yield, 96%; b. p. 114°/0·05 mm., n_D^{16} 1·5732; purity, 96%) (Found : C, 79·5; H, 5·8. Calc. for $C_{14}H_{12}O_2$: C, 79·2; H, 5·7%) was prepared from diphenyl-methyl chloride (20 g.), sodium formate (15 g.), and formic acid (20 g., 80%).

The purity of the esters was checked by estimation of the acid produced on complete hydro-lysis and found to be *ca.* 100% except where stated.

The experimental procedure has been described (Parts I and II). The results are tabulated.

DISCUSSION

The hydrolyses have the kinetic form, rate $\propto$ [H⁺][ester]. The rates for diphenyl-methyl benzoate, acetate, and formate relative to that of the 2 : 4 : 6-trimethylbenzoate are 0·2, 1·6, and 11, respectively, and the values of $\log_{10}$ $(10^6 k_1/c_A)$ $(k_1$ in sec.$^{-1})$ at 100°

* Part IV, *J.*, 1955, 4020.

[1] Stimson, *Nature*, 1955, **175**, 47; Parts I—IV, *J.*, 1954, 2848; 1955, 2010, 2673, 4020.
[2] Bunton and Wood, *J.*, 1955, 1522.
[3] Bunton, Comyns, Graham, and Quayle, *J.*, 1955, 3817.
[4] Dostrovsky and Klein, *J.*, 1955, 791.
[5] Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686.

are 3·9, 3·2, 4·1, and 4·9 (estimated) in 60% acetone for the 2 : 4 : 6-trimethylbenzoate, benzoate, acetate, and formate, respectively. In view of the resistance to hydrolysis generally found for 2 : 4 : 6-trimethylbenzoic esters of primary alcohols, *i.e.*, by mechanism $A_{AC}2$, the high rate for the diphenylmethyl ester indicates the incursion of mechanism $A_{AL}1$. If the rate of hydrolysis of diphenylmethyl esters by mechanism $A_{AL}1$ is taken as

First-order rate constants (k_1) for hydrolysis in aqueous acetone.
(C_A and C_E are the concentrations of hydrochloric acid and ester respectively.)

Solvent (% by vol.)	Temp.	$10^2 C_A$ (mole/l.)	$10^2 C_E$ (mole/l.)	$10^3 k_1$ (min.$^{-1}$)	$10 k_1/C_A$ (min.$^{-1}$ l. mole^{-1})	E (kcal./ mole)	$\log_{10} A$ (sec.$^{-1}$ mole^{-1} l.)	$\Delta S^{\ddagger}$ (cal./mole/ deg.)
Diphenylmethyl 2 : 4 : 6-trimethylbenzoate								
80	109·2°	0·81	1·78	7·1	8·8			
	97·1	1·70	2·10	4·0	2·37	30·4	15·8	11·4
		1·21	2·12	2·86	2·36			
		0·98	2·34	2·45	2·50			
	85·1	1·95	2·12	1·10	0·56	31·2		
		1·30	2·18	0·75	0·57			
Diphenylmethyl benzoate								
80	97·1	1·30	2·72	0·62	0·47			
	85·3	1·16	1·74	0·127	0·110	32·1	15·9	11·8
60	111·3	1·54	1·42	4·8	3·1			
	108·6	1·68	1·40	4·2	2·5			
	97·1	1·54	1·36	1·04	0·67	30·0		
		1·36	1·40	0·99	0·72	31·2	15·1	8·2
	84·5	1·68	1·40	0·29	0·17	30·4		
		1·54	1·42	0·25	0·16			
		1·50	1·42	0·26	0·17			
		1·54	1·36	0·23	0·15			
Diphenylmethyl acetate								
80	109·3	0·88	2·15	1·33	15·1			
	97·1	4·07	1·63	6·3	3·86	31·2	16·3	13·6
	84·8	4·07	1·63	1·68	1·03	28·9		
60	109·2	0·91	2·20	16·6	18·2			
	97·1	2·50	4·03	12·2	4·9	30·0	15·7	11·0
		0·96	1·03	4·55	4·8			
		1·72	2·21	8·7	5·1			
	85·6	1·11	2·25	1·74	1·57	26·5	13·6	1·4
		1·03	2·44	1·63	1·59			
	73·1	1·30	2·24	0·54	0·42	26·0		
	70·7	0·98	2·37	3·30	0·338	25·4	12·9	−1·4
	50·0	2·50	4·03	0·096	0·0384	23·1	11·4	−8·2
40	71·9	2·14	1·77	1·8	0·85			
	50·0	2·25	1·77	0·22	0·098	21·8	11·0	−10·0
Diphenylmethyl formate								
60	97·1	1·04	1·31	36·4	35·1			
		0·52	2·51	18·8	36·1			
	85·0	0·86	1·74	13·0	15·2	18·5	9·8	−16·0
	72·4	1·00	2·24	5·8	5·8	18·7		

E is calculated from the temperature and the mean of the corresponding rates from the line on which it is quoted with the next higher temperature (where it is *ca.* 12° higher) and the corresponding mean rate. For diphenylmethyl benzoate the values 30·0 and 31·2 are obtained from the rate at 97° with those at 111° and 108° respectively. The reliability of E is *ca.* 0·5 kcal./mole.

approximately that of the 2 : 4 : 6-trimethylbenzoate, hydrolysis of these esters by $A_{AL}1$ will be comparable in rate with that of acetates by $A_{AC}2$, for which the above value [6] is 4·1, and slower than that of formates by $A_{AC}2$, for which the figure [6] is 5·3 (calc.). By an argument analogous to that used in Part III, this indicates that the mechanism is predominantly $A_{AL}1$ in the case of the benzoate and $A_{AC}2$ for the formate, in agreement with the results of Day and Ingold.[5] In the case of diphenylmethyl acetate hydrolyses by the two mechanisms are likely to be of comparable rate. This situation is reflected in the activation energy, which for diphenylmethyl 2 : 4 : 6-trimethylbenzoate and benzoate is of

[6] Newling and Hinshelwood, *J.*, 1936, 1359; Timm and Hinshelwood, *J.*, 1938, 869; Davies and Evans, *J.*, 1940, 340.

the order of 30 kcal./mole and for the formate 18·5 kcal./mole, the value [7] usually found for $A_{AC}2$ reactions. The kinetics of hydrolysis of diphenylmethyl acetate do not follow the Arrhenius equation. In 60% acetone, E, calculated from rates at successive temperatures, falls from 30 kcal./mole at 97° to 23 kcal./mole at 50°. This is the behaviour that would be found for two simultaneous reactions of the same kinetic type with considerably different activation energies. The value of E is also different for hydrolyses in solvents of different composition. The values of $\log_{10} A$ and $\Delta S^{\ddagger}$ (cf. Part I) vary in a complementary manner.

It is also noteworthy that, although the diphenylmethyl halides undergo S_N1 reactions faster than the corresponding *tert.*-butyl compounds do, the hydrolyses of diphenylmethyl esters by $A_{AL}1$ are slightly slower (a factor of 0·6 in the case of the 2 : 4 : 6-trimethylbenzoate) than those of *tert.*-butyl esters.[1] Lack of solubility of the 2 : 4 : 6-trimethylbenzoate and benzoate prevents the investigation of their hydrolyses in more aqueous solvents.

[7] Cf. ref. 6; also Smith and Steele, *J. Amer. Chem. Soc.*, 1941, **63**, 3466; Tommila and Hinshelwood, *J.*, 1938, 1806.