*The Kinetics of Alkyl–Oxygen Fission in Ester Hydrolysis. Part III.** tert.-*Butyl Benzoate in Aqueous Acetone.*

By V. R. Stimson.

[Reprint Order No. 6235.]

The kinetics of the acid-catalysed hydrolysis of *tert.*-butyl benzoate in aqueous acetone have been studied. The Arrhenius parameters E and A are different from those found for hydrolysis by mechanism $A_{AC}2$ but are like those found for the hydrolysis of *tert.*-butyl 2 : 4 : 6-trimethylbenzoate (Part II *). It is suggested that these results are due to the operation of mechanism $A_{AL}1$.

Two mechanisms for the acid-catalysed hydrolysis of *tert.*-butyl benzoate in aqueous solvents are inherently likely, namely, $A_{AC}2$ and $A_{AL}1$. Changes in R of R'·CO·OR do not greatly affect the rate of hydrolysis by $A_{AC}2$ but in general the rate is slightly decreased by an increase in the number of alkyl groups on the alkyl carbon atom (Timm and Hinshelwood, *J.*, 1938, 869; Newling and Hinshelwood, *J.*, 1936, 1358; Hammett, "Physical Organic Chemistry," McGraw-Hill, 1940, p. 213), whereas *tert.*-alkyl acetates and succinates are hydrolysed more rapidly than are the primary alkyl esters (Skrabal, *Monatsh.*, 1926, **47**, 17; Homan, *Rec. Trav. chim.*, 1944, **63**, 181). The rate by mechanism $A_{AL}1$ is expected to be influenced largely by R and very little by R' (Day and Ingold, *Trans. Faraday Soc.*, 1941, **37**, 686). Hence, for *tert.*-butyl benzoate the rate of hydrolysis by $A_{AC}2$ should be comparable with, or perhaps slightly smaller than, that of ethyl benzoate for which $\log_{10} 10^6 k_{100}$ (sec.$^{-1}$) = 1·97 in 60% acetone (Timm and Hinshelwood, *loc. cit.*), and by $A_{AL}1$ comparable with that of *tert.*-butyl 2 : 4 : 6-trimethylbenzoate for which this figure is 4·1 (Part II *), so that this ester should be hydrolysed mainly if not wholly by $A_{AL}1$. For uncatalysed alcoholysis Cohen and Schneider (*J. Amer. Chem. Soc.*, 1941, **63**, 3382) have shown that alkyl–oxygen fission is involved, and Bunton has also established this for the acid-catalysed reaction (Ingold, "Structure and Mechanism in Organic Chemistry," G. Bell and Sons, 1953, p. 780). The present work shows that the hydrolysis

* Part II, *J.*, 1955, 2010.

of *tert.*-butyl benzoate has kinetic features unlike those found for hydrolysis by $A_{AC}2$ but very like those found in the case of *tert.*-butyl 2 : 4 : 6-trimethylbenzoate for which only $A_{AL}1$ is likely, and it is suggested that these features are characteristic of mechanism $A_{AL}1$.

First-order rate constants (k_1) for the hydrolysis of tert.*-butyl benzoate in aqueous acetone.*

(C_A and C_E are the concentrations, in moles/l., of hydrochloric acid and ester, respectively.)

Acetone (% by vol.)	Temp.	10^2C_A	10^2C_E	10^3k_1 (min.$^{-1}$)	$10k_1/C_A$ (min.$^{-1}$ l. mole^{-1})	Acetone (% by vol.)	Temp.	10^2C_A	10^2C_E	10^3k_1 (min.$^{-1}$)	$10k_1/C_A$ (min.$^{-1}$ l. mole^{-1})
50	97·1°	1·17	1·78	11·2	9·6	60	,,	0·68	2·74	4·7	6·9
60	97·1	2·10	3·45	13·3	6·4	,,	,,	0·38	2·19	2·7	7·1
,,	,,	1·49	1·82	10·3	6·9	,,	84·3°	1·09	2·06	1·82	1·67
,,	,,	1·19	1·70	7·9	6·6	,,	,,	71·2	1·56	1·87	0·53	0·34
,,	,,	1·13	1·47	7·9	7·0	80	97·1	1·13	1·58	4·6	4·1
,,	,,	1·10	2·16	7·1	6·5	,,	84·3	1·10	2·08	1·04	0·95
,,	,,	1·09	3·71	7·4	6·8	90	97·1	1·14	1·86	3·8	3·3
,,	,,	0·83	2·09	5·6	6·8	95	97·1	1·45	1·83	5·3	3·7

Experimental.—*tert.*-Butyl benzoate (preparation by Mr. E. J. Watson) (Found : C, 73·9; H, 7·9. Calc. for $C_{11}H_{14}O_2$: C, 74·0; H, 7·9%), prepared by the method of Norris and Rigby (*J. Amer. Chem. Soc.*, 1932, **54**, 2099), who report b. p. 96°/2 mm. n_D^{25} 1·4896, had b. p. 50°/0·5 mm., n_D^{24} 1·4900. Pfannl (*Monatsh.*, 1911, **32**, 513) reports b. p. 94°/10 mm. and Bender (*J. Amer. Chem. Soc.*, 1951, **73**, 1626) gives b. p. 67—68°/1 mm., n_D^{25} 1·4890. The purity, calculated from the titre on complete hydrolysis, was 99·5%. The experimental procedure has been described in Parts I (*J.*, 1954, 2848) and II (*loc. cit.*).

Results and Discussion

The hydrolysis of *tert.*-butyl benzoate in aqueous acetone accurately follows first-order kinetics and the rate constants (k_1) are proportional to the concentration of the acid catalyst

Fig. 1.

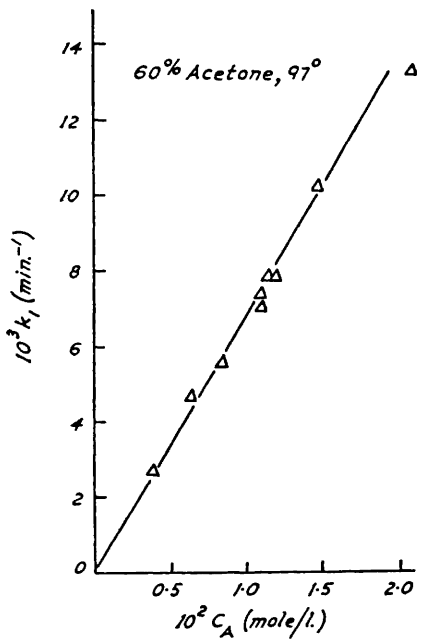
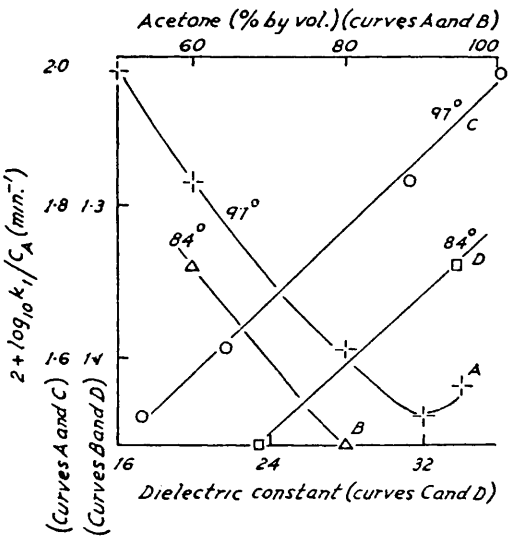


Fig. 2.



and independent of that of the ester (see Table). No significant uncatalysed reaction was detected (cf. Fig. 1, where the plot of k_1 against C_A passes through the origin). The value of $\log_{10} 10^6k_1/C_A$ (sec.$^{-1}$) in 60% aqueous acetone at 100° is 4·2 (calc.); this represents a rate of reaction more than 100 times that of ethyl benzoate (for which this value is 1·97), and of the ethyl esters of nine variously substituted benzoic acids studied by Timm and

Hinshelwood (*loc. cit.*). On the other hand, the rate is almost identical with that of *tert.*-butyl 2 : 4 : 6-trimethylbenzoate, the factor being 1·17. The Arrhenius equation is accurately followed, the values of $E_{Arr.}$ being 29·2 and 30·0 kcal./mole, and $\log_{10} A_{Arr.}$ (sec.$^{-1}$) 15·3 and 15·6, in 60 and 80% acetone, respectively. These values are quite different from those found for hydrolysis by $A_{AC}2$, *viz.*, 16—20 kcal./mole and 7—8, respectively (Timm and Hinshelwood, *loc. cit.*; Newling and Hinshelwood, *J.*, 1936, 1357; Davies and Evans, *J.*, 1940, 339; Smith and Steele, *J. Amer. Chem. Soc.*, 1941, **63**, 3466), but are closely comparable with those found for *tert.*-butyl 2 : 4 : 6-trimethylbenzoate, *viz.*, 30·5 kcal./mole and 16·1, respectively (Part II), so that in the latter case their unusual magnitudes cannot be attributed to the special nature of the 2 : 4 : 6-trimethylbenzoyl portion of the ester. The variation of rate with solvent composition is similar to that found for *tert.*-butyl 2 : 4 : 6-trimethylbenzoate in aqueous acetone (Part II) and is illustrated in Fig. 2. At both 97° and 84°, $m = 0{\cdot}024$.

The microanalysis was carried out by Dr. W. Zimmermann, of C.S.I.R.O., Melbourne.

New England University,
Armidale, N.S.W., Australia. [*Received, March 14th*, 1955.]