Preparation and Hydrolysis of Some Esters of 2 : 4 : 6-Triphenylbenzoic Acid. Part II. The Mechanisms of Hydrolysis.*

By C. A. BUNTON, A. E. COMYNS, J. GRAHAM, and J. R. QUAYLE.

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The reactions of methyl and *tert.*-butyl 2 : 4 : 6-triphenylbenzoates have been followed kinetically in aqueous methanol and in aqueous dioxan under initially neutral conditions and in the presence of acids and bases. By the use of ^{18}O as tracer the positions of bond fission have been determined.

With the methyl ester bimolecular attack on both the acyl- and the alkyl-carbon atom is observed in the presence of alkali, but the *tert.*-butyl ester gives alkyl–oxygen bond fission, with formation of a carbonium ion, under all conditions investigated.

Qualitative observations have been made on the rates of hydrolysis of other esters of this acid.

The reactions of 2 : 4 : 6-triphenylbenzoic acid in the presence of mineral acid have been examined chemically and isotopically.

This work provides examples of all the present known mechanisms of carboxyl esterification and hydrolysis. It illustrates the powerful steric hindrance of the *o*-phenyl groups to nucleophilic attack on the acyl-carbon atom and shows that this effect does not operate on the alkyl-carbon atom.

THE availability of a number of esters of 2 : 4 : 6-triphenylbenzoic acid (Graham and Quayle, Part I *) has made possible a mechanistic study of the reactions of these compounds in aqueous methanol and in aqueous dioxan. The choice of solvents was dictated by solubility requirements.

Preliminary kinetic experiments on the reactions of primary and secondary alkyl 2 : 4 : 6-triphenylbenzoates in aqueous 95% methanol showed these compounds to be unusually resistant to nucleophilic attack under both acid and alkaline conditions, whereas

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* Part I, preceding paper.

the *tert.*-butyl ester was solvolysed in neutral or alkaline solutions at a rate independent of the alkali concentration, but dependent on the acid concentration.

The resistance of the esters of the primary and secondary alcohols to reaction in alkaline and dilute acidic media, conditions which normally lead to bimolecular attack on the acyl-carbon atom (mechanisms $B_{AC}2$ and $A_{AC}2$; Day and Ingold, *Trans. Faraday Soc.*, **1941**, **37**, 686), is largely due to the powerful steric hindrance of the two *o*-phenyl groups. The *tert.*-butyl ester shows no such resistance to solvolysis; in fact its solvolysis rates are qualitatively similar to those of other *tert.*-butyl esters. It appears that this ester undergoes solvolysis by mechanisms independent of bimolecular attack on the acyl-carbon atom, and isotopic experiments prove alkyl–oxygen bond fission.

In concentrated sulphuric acid 2 : 4 : 6-triphenylbenzoic acid and its esters give 1 : 3-diphenylfluorenone (Part I). However, in dilute hydrochloric acid in aqueous dioxan a very slow oxygen exchange between the acid and water is observed, presumably occurring by the mechanism $A_{AC}2$, which is subject to the steric hindrance of the *o*-phenyl groups.

It appears therefore that the esters of 2 : 4 : 6-triphenylbenzoic acid provide a suitable system for a study of some of the less readily realisable mechanisms of ester hydrolysis, and a detailed study has been made of the kinetic form and the position of bond fission of the methyl and the *tert.*-butyl ester in aqueous methanol and aqueous dioxan, and qualitative observations have been made on the reactions of the esters of various primary and secondary alcohols in aqueous methanol.

EXPERIMENTAL

Preparation of Materials.—Methyl, ethyl, *n*-propyl, *iso*propyl, *iso*butyl, and *tert.*-butyl 2 : 4 : 6-triphenylbenzoate were prepared and purified by the methods described in Part I.

Solvents.—Methanol was purified and dried by Lund and Bjerrum's method (*Ber.*, **1931**, **64**, 210). The aqueous methanol used as solvent was prepared by adding 5 vols. of water to 95 vols. of methanol.

Dioxan was purified as described by Vogel ("Practical Organic Chemistry," Longmans Green, **1948**, p. 175). The aqueous dioxan was prepared by adding 3 vols. of water to 7 vols. of dioxan.

Kinetic Measurements.—Kinetic runs were followed in sealed tubes. Thick-walled Pyrex test tubes were used for kinetic runs under acidic and initially neutral conditions, and for alkaline runs in aqueous methanol. This procedure was not satisfactory for the alkaline runs, as prolonged heating at high temperatures caused considerable attack of the alkali on the glass: control tests were carried out and a correction was made for this attack. This, of necessity, reduced the accuracy of the rate measurements in alkaline methanol, and metal containers were investigated.

The most satisfactory metal was found to be silver, and containers with suitable side-arms for the addition and removal of the solutions were manufactured by Messrs. Johnson and Matthey to a design of Dr. Budd. The side-arms of the filled tubes were sealed in an oxy-coal gas flame and were opened by cutting off the tips. Thus the difficulties were removed and silver tubes were used in all the alkaline hydrolyses in aqueous dioxan.

Kinetic runs were followed by acid–alkali titration in absence of carbon dioxide, either by an indicator method (bromothymol-blue), with bromothymol-blue as a colour standard for sodium triphenylbenzoate, or by a potentiometric method with a glass electrode. The latter method, being free from subjective errors, was preferred, and was used in the later work.

Examples of kinetic runs on the methyl and *tert.*-butyl esters are tabulated. $(a - x)$ and $(b - x)$ are the respective concentrations of ester and OH^- at various times.

Alkaline hydrolysis of methyl 2 : 4 : 6-*triphenylbenzoate in aqueous dioxan at* 120°.

[Ester] = 0·0462M, [OH^-] = 0·0404M. Samples of 5·11 c.c. were taken, added to 5 c.c. of 0·07N-H_2SO_4, and titrated with 0·0125N-NaOH.

Time (hr.) ...	—	16·7	40·5	64·5	88·7	113·5	151	175	176	99·2	251
Titre (c.c.) ...	3·6, 3·7	7·4	11·3	11·8	13·4	14·7	16·5	16·8	17·2	18·0	18·4
$\log \frac{a}{b}\left(\frac{b-x}{a-x}\right)$	—	0·016	0·046	0·051	0·074	0·101	0·161	0·179	0·203	0·283	0·32
10^5k_2	—	8·7	10·4	7·2	7·6	8·2	9·7	9·3	10·5	13·0	11·6

Mean value of 10^5k_2 = 9·0 mole^{-1} l. sec.$^{-1}$.

(Value from slope of log $[(b - x)/(a - x)]$ against t, 10^5k_2 = 11·3 mole^{-1} l. sec.$^{-1}$.)

Neutral hydrolysis of tert.*-butyl 2 : 4 : 6-triphenylbenzoate in aqueous dioxan at* 135°.

[Ester] = 0·047M. Samples of 5·15 c.c. were taken and titrated with 0·01N-NaOH.

Time (hr.) ...	0	1·6	2·5	4·0	5·5	7·0	8·0	23·2	25·7	29·7	47·2	55·2
Titre (c.c.) ...	0·3	2·2	3·4	4·6	6·1	7·1	7·8	15·7	16·5	17·5	22·7	23·2
$\log[a/(a-x)]$	—	0·036	0·060	0·085	0·119	0·144	0·161	0·440	0·481	0·539	1·129	1·270
10^5k_1	—	1·44	1·53	1·35	1·38	1·32	1·28	1·21	1·20	1·16	1·53	1·45

Mean value of $10^5k_1 = 1{\cdot}35$ sec.$^{-1}$.
[From the slope of log $(a - x)$ against t, $10^5k_1 = 1{\cdot}39$ sec.$^{-1}$]

Qualitative estimates of the reactivities of the ethyl, *n*-propyl, *iso*propyl, and *iso*butyl esters in aqueous 95% methanol were made by measuring the amount of acid produced in 72 hr. at 118·5°. Allowance was made for the attack of the alkali on the glass. The alkali was *ca.* 0·05M, and the ester was *ca.* 0·02M. The % reactions were: Me 61; Et 17; β-methylated, Pr^n 6·5, Bu^i 6; α-methylated, Pr^i 3, Bu^t 72, 72·5.

In view of the possibility of the reaction, $R{\cdot}CO_2R + OMe^- \rightleftharpoons R{\cdot}CO_2Me + OR^-$, occurring in 95% methanol more precise determinations of the reactivities of the various esters in this sytem were not undertaken.

Under initially neutral and acid conditions (N/20-benzenesulphonic acid), in aqueous methanol, no solvolysis was detected for the methyl, ethyl, *n*-propyl, *iso*propyl, and *iso*butyl esters after 48 hr. at 118·5°. Prolonged heating resulted in explosion of the glass tubes, presumably owing to formation of dimethyl ether from the aqueous 95% methanol.

No hydrolysis of the methyl ester was observed in aqueous 70% dioxan in initially neutral and acidic conditions during 11 days at 120°.

A summary of the kinetic results is tabulated.

Tracer Studies.—In all tracer studies the water was isotopically enriched, and the ester, or acid, was initially of normal abundance. The low solubilities of the esters in the aqueous solvents, and their high molecular weights, precluded the isolation of the alcohol product in quantities sufficient for an isotope analysis, and such an isolation would have been valueless in reactions in aqueous methanol. Therefore the isotopic abundance of oxygen in the 2 : 4 : 6-triphenylbenzoic acid product was determined.

TABLE 1. *Solvolyses in aqueous methanol.*

(i) *Neutral and alkaline reactions.* Temp., 118·5°. Solvent, aqueous 95% methanol.

(*a*) Me ester + OMe$^-$: 10^5k_2 = 5·5, 6·7, 5·7 mole^{-1} l. sec.$^{-1}$.
(*b*) Bu^t ester + 95% MeOH : 10^6k_1 = 5·25 sec.$^{-1}$.*
,, + 0·0333M-H_2O in MeOH : 10^6k_1 = 2·91 sec.$^{-1}$.*
,, + 0·0555M-H_2O in MeOH : 10^6k_1 = 2·94 sec.$^{-1}$.*
,, + OR$^-$(R=H or Me) : 10^6k_1 = 4·9 sec.$^{-1}$.

* Extrapolated to zero time.

(ii) *Acid-catalysed reactions of* tert.*-butyl ester.*

Solvent, 95% methanol.			Solvent, methanol with small quantities of water.			
Temp.	[H$^+$]	10^4k_A (mole^{-1} l. sec.$^{-1}$)	Temp.	[H_2O]	[H$^+$]	10^3k_A (mole^{-1} l. sec.$^{-1}$)
80·0°	0·0540	23·8	80·0°	0·0344	0·0516	11·8
,,	0·0406	24·3	65·2	0·0333	0·0687	2·37
70·1	0·0585	7·20	,,	0·0555	0·0509	2·28
,,	0·0535	7·25				

$k_1 = k_A[H^+]$.

TABLE 2. *Hydrolyses in aqueous 70% dioxan.*

[OH$^-$]	Temp.	10^7k_1 (sec.$^{-1}$)	[OH$^-$]	Temp.	10^5k_2 (mole^{-1} l. sec.$^{-1}$)
Bu^t *ester*			Me *ester*		
—	101·2°	3·76	0·055	120·0°	11·3
—	120	24·4			
—	135	139			
0·050	120	22·0			

After reaction (which was usually not carried to completion because of the low reaction rates), most of the organic solvent was removed under reduced pressure, and the triphenylbenzoic acid and unchanged ester were separated. The acid was converted into its silver or calcium salt, and the salt, after intensive drying in a high vacuum, was decarboxylated by heat. The silver salt was used for the decarboxylation of the acid obtained from hydrolysis in aqueous dioxan, and the calcium salt for most of the products of reactions in aqueous methanol.

The oxygen isotopic abundance of the carbon dioxide was determined by mass-spectrometry. The ratio of abundances, R, of masses 44 and 46 (corresponding to $^{12}C^{16}O^{16}O$ and $^{12}C^{16}O^{18}O$), was determined. Then if α is the atom % abundance of ^{18}O in the carbon dioxide, then $\alpha = 100/(2R + 1)$ atoms %.

The isotopic abundances were always compared with a standard sample of gaseous carbon dioxide, prepared by the decarboxylation of normal 2 : 4 : 6-triphenylbenzoic acid. The values of isotopic abundances quoted are the excess abundance of a sample above that of a normal sample.

The isotopic abundance of the water used was in general determined by equilibration with gaseous carbon dioxide, followed by mass spectrometry of the carbon dioxide. The isotopic abundance, α, of the water is given by $\alpha = 100/(KR + 1)$, where $K = 2{\cdot}076$ at 25°.

The isotopic abundances of one sample of enriched water (that used in the blank tests and solvolyses of the *tert.*-butyl esters in aqueous methanol) was estimated from a density determination carried out by Dr. D. R. Llewellyn.

The isotopic analyses on samples obtained from reactions in aqueous methanol were (with two exceptions, experiments W5 and X18) carried out by the Mass Spectrometer Group of the Atomic Energy Research Establishment, Didcot. Other isotope analyses were carried out on a 180° mass spectrometer of conventional design.

Under all conditions control experiments were carried out to ensure that the presence or absence of tracer was not due to extraneous exchange, or to isotopic discrimination, in the isolation or decarboxylation of the triphenylbenzoate. The standard normal sample of acid had an excess isotopic abundance (determined by decarboxylation) of 0·002 atoms % greater than that of normal cylinder carbon dioxide.

The results of the tracer experiments are in Tables 3—5.

TABLE 3. *Reactions in* 95% *methanol.*

Experiment		^{18}O abundance (atoms % excess) :		O_2 derived
No.	Description	in H_2O	in acid isolated	from H_2O (%)
B1	Untreated acid	—	0·00	—
B2	Control for B3; 130°	0·80	0·001	—
B3	Neutral; Bu^t ester; 3 days; 130°	0·80	0·001	—
B4	0·08M-Acid; Bu^t ester; 1½ days; reflux	0·80	0·00	—
B5	Control for B4; reflux	0·80	0·00	—
B6	Control for W5 & X18; 120°	0·80	0·00	—
W5	0·064M-NaOH; Me ester; 13 days; 120° *	0·532	0·033	6·2
X18	As W5; 9 days *	1·156	0·075	6·5

* In Ag tube.

Isolation of Dimethyl Ether.—An attempt was made to isolate dimethyl ether after reaction of the methyl ester (1·04 g.) in aqueous 95% methanol with M/30-alkali at 120° for 40 days. As this reaction was carried out under kinetic conditions the quantity of ether formed was expected to be small. The ether was fractionated through a low-hold-up column with a gas take-off.

TABLE 4. *Blank tests in aqueous* 70% *dioxan at* 120°.

Experiment			^{18}O abundance (atoms % excess):		O_2 derived from
No.	Description	Days	in H_2O	in acid or ester	solvent (%)
W20	Neutral Na salt	11	0·300	0·001	—
W21	Alkaline Na salt	10	0·300	0·002	—
W2	Acid alone	100	0·532	0·002	—
W3	Acid + 0·7M-HCl	100	0·532	0·142	26·5
X4	,,	100	1·156	0·315	27
X10	Me ester + 0·07N-NaOH	13	,,	0·133, 0·162 *	11·5, 14

* Ester isolated and pyrolysed (both expts.).

The distillate contained some material of low volatility, which was removed by static distillation in a high vacuum. The purified ether had M 48 and comprised 80% of the original distillate. The purification by static distillation and the measurement of molecular weight by vapour density were carried out by Dr. Joan Banus.

The yield of ether was 45%. A parallel experiment on a solution of dimethyl ether gave an overall recovery of *ca.* 60%. Although these results are only qualitative they show that some dimethyl ether is formed by bimolecular attack of the methoxide ion on the alkyl-carbon atom of methyl 2 : 4 : 6-triphenylbenzoate.

TABLE 5. *Hydrolyses in aqueous dioxan.* (Excess abundance of ^{18}O in H_2O, 1·156%.)

Expt. no.	Concn. (%) of dioxan	Conditions	[Ester] (M)	^{18}O Abundance in acid (atoms % excess)	O_2 derived from solvent (%)
Bu^t *ester*					
X1	70	0·02M-H_2SO_4 (18 hr.)	0·030	0·00	—
X2	"	Neutral (14 days)	0·037	0·00	—
X11	"	Alkali (14 days)	0·037	0·003	—
Me *ester*					
X8	70	0·07M-NaOH (13 days)	0·043	0·716	62
X5	"	" "	0·060	0·684	59
X6	"	0·049N- "	0·060	0·653	56·5
X7	"	0·042N- "	0·060	0·638	55
X12	75	0·025N-NaOH (14 days)	0·027	0·653	56·5
X13	73	" "	"	0·653	56·5
X14	71	" "	"	0·644	55·5
X15	70	" "	"	0·648	56
X16	69	" "	"	0·638	55

DISCUSSION

Position of Bond Fission.—In principle the position of bond fission in ester hydrolysis can be determined unambiguously by the use of ^{18}O as a tracer. This classic method has frequently been used (Polanyi and Szabo, *Trans. Faraday Soc.*, 1934, **30**, 508; Datta, Day, and Ingold, *J.*, 1939, 838), with isolation and isotopic assay of the alcohol product. In the present work it has been necessary to follow the tracer in the acid product; alkyl–oxygen fission gives an acid containing no isotopic tracer.

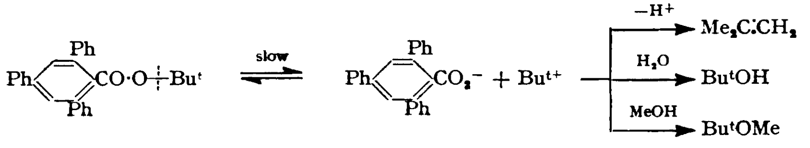
Bimolecular acyl–oxygen bond fission may give an exchange between the oxygen atoms of the water and the carbonyl-oxygen atoms of the ester (Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626).

In the hydrolysis of methyl 2 : 4 : 6-triphenylbenzoate in alkaline aqueous dioxan the ester was recovered from a partial hydrolysis, and was found to be isotopically enriched (Expt. X10), showing that oxygen exchange of the methyl ester occurred during hydrolysis. In view of Bender's similar observations on the benzoates (*loc. cit.*), we did not feel justified in raising this to a quantitative level. It is because of this exchange reaction of the ester molecule that the isotopic abundances of the methyl 2 : 4 : 6-triphenylbenzoate exceeds half that of the water (Experiments X5—8, 12—16 incl.).

The results for the methyl ester in aqueous dioxan show that the predominant fission was of the acyl–oxygen bond. They do not exclude the existence of a small amount of alkyl–oxygen bond fission in the alkaline hydrolysis, since the effect of this mechanism in giving no tracer in the acid could be masked by the oxygen exchange of the ester.

An increase in alkali concentration gives a small increase in the isotopic abundance in the isolated acid, whereas an increase in the water content of the solvent has the opposite effect. This dependence on the water content of the solvent may be due to a small amount of alkyl–oxygen bond fission (by mechanisms $B_{AL}2$ or $B_{AL}1$), which would probably be favoured by an increase in the water content of the solvent.

Isotopically normal acid is obtained in the solvolyses of *tert.*-butyl 2 : 4 : 6-triphenylbenzoate in both aqueous dioxan and aqueous methanol, proving alkyl–oxygen bond fission. Preliminary experiments (carried out by Mr. B. Stephenson) showed that considerable amounts of *iso*butene were formed in the alkaline solvolyses, and as the kinetic measurements show no rate acceleration by alkali we may depict the solvolysis of this ester in initially neutral and alkaline solutions thus :



The reactions of the methyl 2 : 4 : 6-triphenylbenzoate in aqueous methanol in the presence of methoxide ion are complicated by the co-existence of hydrolysis and methanolysis.

Four simultaneous reactions are possible :

Acyl–oxygen bond fission :

(*a*) $\mathrm{R{\cdot}CO} \vdots \mathrm{{-}OMe} + {}^{18}\mathrm{OH}^- \longrightarrow \mathrm{R{\cdot}CO{\cdot}{}^{18}O}^- + \mathrm{Me{\cdot}OH}$

(*b*) $\mathrm{R{\cdot}CO} \vdots \mathrm{{-}OMe} + \mathrm{MeO}^- \longrightarrow \mathrm{R{\cdot}CO{\cdot}OMe} + \mathrm{MeO}^-$

Alkyl–oxygen bond fission :

(*c*) $\mathrm{R{\cdot}CO{\cdot}O{-}} \vdots \mathrm{Me} + {}^{18}\mathrm{OH}^- \longrightarrow \mathrm{R{\cdot}CO{\cdot}O}^- + \mathrm{Me{}^{18}OH}$

(*d*) $\mathrm{R{\cdot}CO{\cdot}O{-}} \vdots \mathrm{Me} + \mathrm{MeO}^- \longrightarrow \mathrm{R{\cdot}CO{\cdot}O}^- + \mathrm{MeOMe}$

Only reactions (*a*), (*c*), and (*d*) will give identifiable products, as reaction (*b*) in this special case merely regenerates the methyl ester. Only reaction (*a*) introduces tracer into the acid. Experiments W5 and X18 show that in aqueous methanol fission of the alkyl–oxygen bond predominates, although it does not disclose whether the reagent is the hydroxide or the methoxide ion ; and, as there is no precise knowledge of the position of the equilibrium under our conditions, for the reaction, $\mathrm{MeOH} + \mathrm{OH}^- \rightleftharpoons \mathrm{MeO}^- + \mathrm{H_2O}$ (cf. Caldin and Long, *J.*, 1954, 3737), the relative concentrations of these ions are unknown. Isolation of dimethyl ether from the reaction of the methyl ester in alkaline aqueous methanol at 120° shows that reaction (*d*), attack of the methoxide ion on the alkyl-carbon atom, does occur. It may be that in aqueous 95% methanol all the isotopically normal acid is produced by methanolysis, and that hydrolysis gives attack on the acyl-carbon atom only, for the isolation experiment was not sensitive enough to test this. These experiments give no information on the attack of the methoxide ion on the acyl-carbon atom (reaction *b*), as this could be observed only by isotopic labelling of the methyl group on carbon or hydrogen.

The formation of dimethyl ether by the attack of methoxide ion in methyl alcohol, on the alkyl-carbon atom of methyl benzoate (Bunnett, Robinson, and Pennington, *J. Amer. Chem. Soc.*, 1950, **72**, 2328), shows that bimolecular attack on the methyl group of a methyl ester can occur under conditions similar to those of our experiments in aqueous 95% methanol.

Kinetic Form and Mechanism of Reaction.—The 2 : 4 : 6-triphenylbenzoates of primary and secondary alcohols studied in this work decompose only in the presence of alkali. We can therefore exclude, for them, all mechanisms which involve ionisation of the neutral ester molecule or reaction of its protonated species.

In aqueous dioxan the values of the second-order rate coefficients for the alkaline hydrolysis of the methyl ester, together with the tracer experiments, show that the predominant mechanism is $B_{\mathrm{AC}}2$. In this solvent the steric hindrance by the two *o*-phenyl groups is sufficient to make the acyl-carbon atom relatively insensitive to nucleophilic attack, but it is insufficient to make this attack slower than ionisation of a methyl carbonium ion from the neutral molecule or slower than attack of the hydroxide ion on the alkyl-carbon atom.

The kinetic form of the hydrolysis of *tert.*-butyl 2 : 4 : 6-triphenylbenzoate in neutral and alkaline aqueous dioxan, and the demonstration of alkyl–oxygen bond fission show that the rate-determining step is the ionisation of the neutral ester molecule (mechanism $B_{\mathrm{AL}}1$), a reaction strictly analogous to the well-defined $S_{\mathrm{N}}1$ reactions of alkyl halides.

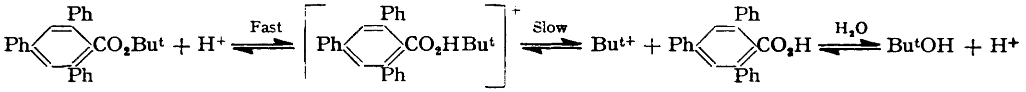
In aqueous 95% methanol reaction rate decreases with increase in the length of the alkyl group for esters of various primary and secondary alcohols : but these measurements were qualitative and their interpretation is complicated by trans-esterification. The last reaction will generate the methyl ester, the most reactive of the group considered, and will therefore reduce any rate differences. The decrease of rate observed is consistent with nucleophilic attack on either the alkyl- or the acyl-carbon atom, and as the tracer results for the alkaline reaction of the methyl ester in this solvent show that both modes of attack occur, attempts to interpret these results quantitatively would not be justified.

In aqueous methanol the solvolysis of *tert.*-butyl 2 : 4 : 6-triphenylbenzoate is not accelerated by the addition of alkali ; in fact the rate in initially neutral solution is slightly greater than the rate in the presence of alkali. A small anticatalytic effect of the hydroxide ion is typical of many S_N1 reactions (Benfey, Hughes, and Ingold, *J.*, 1952, 2494), but this interpretation is complicated by the observation of slight anticatalysis in the neutral reaction. This rate increase in the course of the run (which is not observed with the *tert.*-butyl ester in aqueous dioxan) is presumably due to catalysis by the triphenylbenzoic acid, or by the protons derived from it.

As would be expected, this solvolysis, in which the formation of a carbonium ion from the neutral ester molecule is the rate-determining step, is facilitated by an increase in the water content of the solvent. The effect is not large, suggesting that the methanol molecules are comparable to the water molecules in their ability to solvate the partially formed carbonium ion. This is in marked contrast to the effect of a change of water content in the aqueous dioxan used as solvent in the hydrolysis of triphenylmethyl acetate by mechanism $B_{AL}1$ (Bunton and Konasiewicz, *J.*, 1955, 1354). In this system, where the solvent effect is very marked, the dioxan molecules presumably make very little contribution to the solvation of the partially formed carbonium ion.

In sharp contrast to the primary and secondary alkyl triphenylbenzoates, the *tert.*-butyl ester shows a very marked acid catalysis of solvolysis in aqueous methanol.

The isotopic results prove alkyl–oxygen bond fission by mechanism $A_{AL}1$:



Because of the ease of hydration of *iso*butene under acid conditions no attempt was made to identify an elimination product in this reaction. It would be expected, however, that the carbonium ion would be partitioned between substitution and elimination, as in solvolysis in neutral or alkaline solution.

The effect of a change in the water content of the aqueous methanol solvent is in the opposite direction to that observed for the neutral reaction. The solvent effect in an acid-catalysed ester solvolysis (*e.g.*, $A_{AL}1$) is two-fold, an effect on the pre-equilibrium proton transfer, and one on the breakdown of the protonated ester molecule.

The tendency of hydrochloric acid to donate a proton to a neutral base has been shown to decrease on the addition of small amounts of water to ethanol (Braude and Stern, *J.*, 1948, 1976; and activity measurements); this is probably true also for the addition of small amounts of water to methanol. Therefore the addition of water to methanol will lower the equilibrium concentration of the protonated ester, and hence decrease the reaction rate. In other systems in which the $A_{AL}1$ mechanism is observed (triphenylmethyl and *tert.*-butyl acetates in aqueous dioxan), the rate of decomposition of the protonated ester increases with increase in the water content of the solvent. It seems therefore that in aqueous methanol the water is little more effective than methanol in solvating the partially formed carbonium ion, but is more effective in holding the protons, and that the latter effect in decreasing the rate outweighs the former effect in increasing it.

For the solvolyses of *tert.*-butyl 2 : 4 : 6-triphenylbenzoate the parameters A and E of the Arrhenius equation $k = A\mathrm{e}^{-E/RT}$ are :

In initially neutral aqueous 70% dioxan,

$A = 3{\cdot}2 \times 10^{12}$ sec.$^{-1}$, $E = 32{\cdot}4$ kcal. mole^{-1} (from 3 temp.).

In acidic aqueous 95% methanol,

$A = 3{\cdot}7 \times 10^{15}$ mole^{-1} l. sec.$^{-1}$, $E = 29{\cdot}3$ kcal. mole^{-1} (from 2 temp.).

The activation energy for the ionisation of this tertiary alkyl ester molecule is therefore *ca.* 32 kcal. mole^{-1}, and the value of the activation energy for the acid-catalysed solvolysis is 29·3 kcal. mole^{-1} [cf. the value of *ca.* 30 for the acid-catalysed solvolysis of *tert.*-butyl trimethylbenzoate in aqueous ethanol (Stimson and Watson, *J.*, 1954, 2848), a reaction which presumably involves alkyl–oxygen bond fission]. This suggests that the heat content for the protonation of a tertiary alkyl ester is small compared with the activation energy for the formation of a carbonium ion from it.

These mechanisms and examples of the systems in which they are observed may be summarised as follows :

Acyl–oxygen fission. $B_{AC}2$. Hydrolysis of methyl ester in aqueous dioxan. It also occurs to some extent with this ester in aqueous methanol.

$A_{AC}2$. Observed only in oxygen exchange of the acid in aqueous dioxan.

$A_{AC}1$. Not observed in hydrolysis. Its existence is demonstrated by the formation of 1 : 3-diphenylfluorenone by the action of sulphuric acid on the acid or its esters.

Alkyl–oxygen fission. $B_{AL}1$. The *tert.*-butyl ester in neutral or alkaline solutions.

$B_{AL}2$. Occurs to some extent with the methyl ester in alkaline aqueous methanol. It may not occur with OH^- as the reagent, under these conditions.

$A_{AL}1$. Observed in solvolysis of the *tert.*-butyl ester in acidic aqueous methanol.

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WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER STREET, LONDON, W.C.1.
UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

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