A Stopped-flow Investigation of the Rate of Formation and Disappearance of the 4,4′,4″-Trimethoxytriphenylcarbonium Ion in Dioxan–Water Mixtures

By **H. Nicholson** and **P. A. H. Wyatt,*** Department of Chemistry, The University, Sheffield 10

First-order rate constants and equilibrium extents of conversion are recorded for the formation of the coloured carbonium ion from 4,4′,4″-trimethoxytriphenylmethanol in 0·1M- and 1·0M-HCl solutions in several dioxan–water mixtures, and in $HClO_4$ and $LiClO_4$–$HClO_4$ solutions in the 40 and 60 vol. % dioxan mixtures. The Gibson stopped-flow technique was used for the kinetic measurements.

The acidity function H_R, like H_0, passes through a maximum near the middle of the dioxan–water range, and the rate of attainment of equilibrium passes through a minimum. A minimum is also observed in the rate of approach to equilibrium as the $HClO_4$ concentration is increased at a fixed dioxan–water ratio; but this minimum disappears when the total electrolyte concentration is kept at 1M by additions of $LiClO_4$. In the latter case the rate constant for the ion formation is proportional to the $HClO_4$ concentration and the rate constant for the back reaction is practically independent of it. The function h_R, = antilog$_{10}$($-H_R$), is also nearly proportional to the $HClO_4$ concentration in these $LiClO_4$–$HClO_4$ solutions.

To gain greater insight into the effects of salts upon the ionisation equilibria of indicators, and hence to improve understanding of the differences between certain indicator acidity scales,[1-5] an investigation was projected of the effects of salts upon the rates of the forward and reverse reactions involved. Secondary bases, the ionisation of which involves the rupture of a carbon–oxygen bond at some stage, were chosen for study as being more likely to yield rate constants accessible to our available techniques than simple protonation reactions. It is well known that reactions of this kind can often be followed by conventional techniques in neutral and alkaline media [6-10] and we now report that they can be studied by the stopped-flow technique in acid solution. We also note that Ritchie and his co-workers, in a recent

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investigation of the reactions of carbonium ions with nucleophiles in different solvents, have used the stopped-flow method for their fastest reactions.[11]

Though an apparatus for handling concentrated acids is under construction, the present measurements were all limited to less corrosive solutions (generally 1M or less), thus restricting the bases to the methoxytriphenylmethanols.[12-14] Solubility also imposed an initial limitation on the precision obtainable with aqueous solutions alone and most of the measurements therefore refer to dioxan–water mixtures. Refinements of technique introduced by Mr. M. J. Postle have since removed the difficulties with purely aqueous solutions, but the dioxan–water solvent mixtures still present some special features of interest.

To assist in the interpretation of the kinetic results some measurements of the equilibrium ratio of carbonium ion to alcohol concentration, and hence of the acidity function H_R, have been made for the mixtures used in the kinetic work.

Formulation of the Kinetics.—If the forward and reverse reactions are assumed to take place in one step, the reaction scheme is

$$\mathrm{R_3COH + H^+ \underset{k_b'}{\overset{k_f'}{\rightleftharpoons}} R_3C^+ + H_2O} \qquad (1)$$

but, since the acidity and water activity are both fixed by the medium, the experimental first-order constants, denoted by k_f and k_b, will differ from the primed constants in equation (1) by including the acid and water dependence:

$$\text{Rate of forward reaction} = k_f[\mathrm{R_3COH}] \qquad (2)$$

$$\text{Rate of backward reaction} = k_b[\mathrm{R_3C^+}] \qquad (3)$$

The dependence of the ratio k_f/k_b upon water activity and acidity must of course accord with the known dependence of the equilibrium ratio $[\mathrm{R_3C^+}]/[\mathrm{R_3COH}]$ upon h_R [*i.e.*, antilog$_{10}$ $(-H_R)$].

In cases of this kind, the experimentally determined first-order rate constant, k, is the sum[15] of k_f and k_b, and $(k_f + k_b)$ is obtained for the rate constant whichever way the reaction proceeds, as the integrated rate equations show:

For the appearance of the coloured $\mathrm{R_3C^+}$,

$$\ln([\mathrm{R_3C^+}]_e - [\mathrm{R_3C^+}]) - \ln[\mathrm{R_3C^+}]_e = -(k_f + k_b)t \qquad (4)$$

For its disappearance,

$$\ln([\mathrm{R_3C^+}] - [\mathrm{R_3C^+}]_e) - \ln([\mathrm{R_3C^+}]_i - [\mathrm{R_3C^+}]_e) = -(k_f + k_b)t \qquad (5)$$

$[\mathrm{R_3C^+}]_e$ is the final, equilibrium, concentration of $\mathrm{R_3C^+}$, $[\mathrm{R_3C^+}]$ its concentration at time t, and $[\mathrm{R_3C^+}]_i$ its initial concentration in the second type of experiment. Knowledge of the equilibrium ratio $[\mathrm{R_3C^+}]/[\mathrm{R_3COH}]$ $[=k_f/k_b$, by equating (2) and (3)] then permits the separation of the two constants k_f and k_b.

Although there is no evidence for the presence of the protonated species $\mathrm{R_3COH_2^+}$ in measurable amounts there seems no *a priori* reason why this species should not exist[10] as an intermediate in the formation of the carbonium ion. If this proves to be the case, the experimental values of k_f and k_b can easily be related to the appropriate constants in the following way:

$$k_f = k_{f_1}k_{f_2}/(k_{b_1} + k_{f_2}) \qquad (6)$$

and

$$k_b = k_{b_1}k_{b_2}/(k_{b_1} + k_{f_2}) \qquad (7)$$

The rate constants in equations (6) and (7) refer to the reaction stages as follows:

$$\mathrm{R_3COH + H^+ \underset{k_{b_1}}{\overset{k_{f'_1}}{\rightleftharpoons}} R_3COH_2^+ \underset{k_{b'_2}}{\overset{k_{f_2}}{\rightleftharpoons}} R_3C^+ + H_2O} \qquad (8)$$

The primed constants are second-order constants, which are converted to the unprimed k_{f_1} and k_{b_2} by inclusion of acidity and water activity factors as before. Equations (6) and (7) are arrived at by straightforward algebra, using the condition that $d[\mathrm{R_3COH_2^+}]/dt$ must always be negligibly small (justifying the 'stationary state' approximation) since $[\mathrm{R_3COH_2^+}]$ is always small.

RESULTS

Acidity Functions.—All values of H_R recorded in Tables 1—3 have been calculated from $pK_R = 0{\cdot}66$ at 1·1° and 0·82 at 25°, keeping the standard state reference in pure water.[12,14] Experimental indicator ratios are easily recovered when required from

TABLE 1

H_R Values for HCl in dioxan–water mixtures, based on $pK_R = 0{\cdot}82$ at 25° and 0·66 at 1·1° for the indicator 4,4′,4″-trimethoxytriphenylmethanol

Vol. % dioxan	0·1M-HCl at 25°	0·1M-HCl at 1·1°	1·0M-HCl at 25°	1·0M-HCl at 1·1°
0	1·06	0·90	−0·28	−0·50
20	1·89	1·81	+0·66	+0·52
40	2·52	2·58	0·95	0·92
60	3·24	3·54	1·76	1·94
70	3·53	3·82	1·91	
80	3·80			
90	3·91			
95	3·45			
100	2·69		1·57	

$$H_R = pK_R + \log_{10}[\mathrm{R_3COH}]/[\mathrm{R_3C^+}] \qquad (9)$$

In some cases the $[\mathrm{R_3C^+}]/[\mathrm{R_3COH}]$ ratio at the end of a kinetic experiment has been calculated from the spectrophotometric trace, and H_R values derived from such ratios have been included in the Tables and generally show reasonable agreement with the special determinations.

As with H_0 for 0·1M-HCl solutions in mixtures ranging from 100% water to 100% dioxan,[16] H_R at first increases

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in the positive direction, shows a maximum at about 50 mole %, and then changes in the negative direction (Table 1), but the changes are more marked for the H_R indicators. Similar effects are observed at 1·0M-HCl, but the range is then restricted by incomplete miscibility at high dioxan concentrations. The initial fall in the equilibrium carbonium ion concentration as the water concentration is decreased shows that stabilisation of R_3COH and the solvated proton relative to R_3C^+ must at first outweigh the mass action effect of the water in equilibrium (1). This is probably partly attributable to strong solvation of H_3O^+; there is evidence that the hydroxonium ion is already solvated by three dioxan molecules at only 20 mole % dioxan.[17]

TABLE 2

H_R Values for $HClO_4$ in 40 vol. % dioxan–60% water and in 60 vol. % dioxan–40% water mixtures at 1·1° (pK_R = 0·66)

40 vol. % dioxan	$HClO_4$ molarity	0·0335	0·105	0·132	0·236	0·335	0·426	0·508	0·625	0·628	0·799	0·913	0·951	
	H_R	2·96	2·25	2·08	1·62	1·21	0·92	0·71	0·47	0·43	0·08	−0·13	−0·33	
60 vol. % dioxan	$HClO_4$ molarity	0·100 *	0·102	0·215	0·301 *	0·332	0·500 *	0·500	0·655	0·749 *	0·846	1·000	1·000 *	1·206
	H_R	2·73	2·85	1·99	1·83	1·75	1·32	1·25	0·78	0·58	0·28	−0·08	−0·10	−0·66

* From kinetic measurements.

The variation of H_R with acid concentration was investigated in detail for the 40 and 60% dioxan solutions (Table 2), for which some data [13] are already available at 25°. Significantly larger changes in H_R with concentration are observed at the lower temperature than at 25°, especially in the 60% dioxan solution. (The behaviour is more irregular in aqueous H_2SO_4 solutions.[14]) Though the numbers quoted all refer to the aqueous standard state, graphs of $\log_{10}([R_3C^+]/[R_3COH] - [HClO_4])$ against $[HClO_4]$ were extrapolated back to zero concentration in both 40 and 60% dioxan solutions, thus obtaining [18] −0·96 and −1·35 for pK_R at 1·1° referred to standard states in these two mixtures respectively.

TABLE 3

H_R Values for $LiClO_4$–$HClO_4$ mixtures of total molarity 1·0 or 0·5 in 60 vol. % dioxan–40% water mixtures at 25° and 1·1°

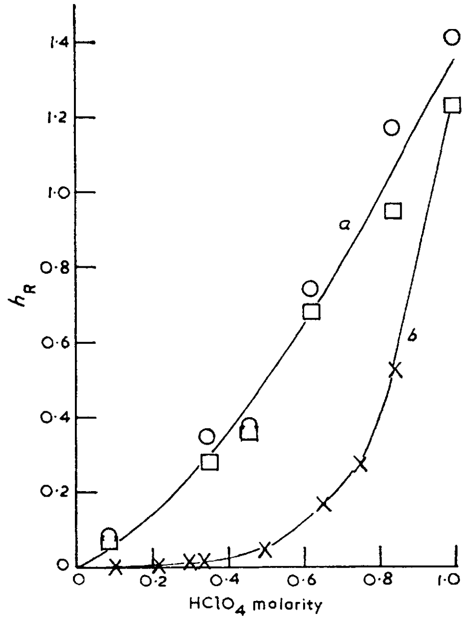
Total molarity 1·0			Total molarity 0·5		
$HClO_4$ molarity	H_R at 25° (pK_R = 0·82)	H_R at 1·1° (pK_R = 0·66)	$HClO_4$ molarity	H_R at 25° (pK_R = 0·82)	H_R at 1·1° (pK_R = 0·66)
1·000	−0·15	−0·09	0·500	1·13	1·25
0·838	−0·07	+0·02	0·500 †	—	1·32
0·820 †	—	0·19(?)	0·400	1·28	1·41
0·620	+0·13	0·17	0·377 †	1·43	1·42
0·458 †	0·42	0·44	0·284	1·48	1·61
0·349	0·46	0·55	0·203	1·55	1·68
0·0855 †	—	1·15	0·106 †	—	1·95
0·0804	1·09	1·17	0·0930	1·98	2·10
			0·0297 †	—	2·29

† From kinetic measurements.

The $LiClO_4$–$HClO_4$ mixtures of constant total anion concentration are of special interest for the interpretation of the kinetics. Because of the similar solvation properties of Li^+ and the proton, solutions of this kind should keep the water activity, and hence the state of hydration of the proton, much more nearly constant as the acid concentration is increased than is the case for a pure acid solution itself.[19] Consequently h_R should vary more linearly with $HClO_4$ concentration in such mixtures, thereby permitting a separation of the acidity from the water activity effect in kinetic experiments. Comparison of curves *a* and *b* in the Figure shows that this certainly is the case, though the dependence for $LiClO_4$–$HClO_4$ mixtures is still not quite linear.

Rate Constants.—Tables 4—8 summarise the results of the kinetic experiments with 4,4′,4″-trimethoxytriphenylmethanol. Rate constants determined during the disappearance of the carbonium ion are marked with an asterisk: in all other cases the rate of appearance of the ion was measured.

Tables 4 and 5 show that increasing the dioxan content of the solvent at a fixed acid concentration accelerates the back reaction from 20 to 70 vol. % dioxan, after which there is some indication of a reduction in rate. The forward reaction, on the other hand, slows down considerably. Since the water activity must be lower in a dioxan mixture than in pure water, the increase in k_f implies that the carbonium ion must be destabilised relative to the transition state as the dioxan concentration increases.



The dependence of h_R upon $HClO_4$ concentration in 60 vol. % dioxan with and without the addition of $LiClO_4$; *a*, $LiClO_4$–$HClO_4$ mixtures of 1M total molarity: ○ 25°, □ 1·1°; *b*, $HClO_4$ solutions without added $LiClO_4$: × 1·1°

Contributing factors could be the increase in electrostatic energy of R_3C^+ (which will be less solvated than the proton and therefore have a relatively small effective radius), and favourable adjustments in the solvation sheath of the proton and alcohol in the transition state.

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TABLE 4

Rate constants in 0·1M-HCl solutions in aqueous dioxan

Vol. % dioxan	Temp.	% R_3C^+ at equilibrium	k (sec.$^{-1}$)	k_{f} (sec.$^{-1}$)	k_{b} (sec.$^{-1}$)
0	1·1°	36·6	12·9 *	4·7	8·2
20	1·1	6·58	9·8 *	0·6	9·2
40	1·1	1·03	14·9 *	0·1	14·8
60	1·1	0·13	32		32
70	1·1	0·06	42		42
0	25·0	36·6	43 *	16	27
20	25·0	8·62	44 *	4	40
40	25·0	1·97	77 *	2	75
60	25·0	0·38	101		101
70	25·0	0·20			~210 †
80	25·0	0·10			~160 †
90	25·0	0·08			88 †

* Disappearance of carbonium ion followed. † Interpolated from Arrhenius plot of data at 3 or 4 temperatures.

TABLE 5

Rate constants in 1·0M-HCl solutions in aqueous dioxan at 1·1°

Vol. % dioxan	% R_3C^+ at equilibrium	k (sec.$^{-1}$)	k_{f} (sec.$^{-1}$)	k_{b} (sec.$^{-1}$)
0	93·5	60	56	4
20	58·0	11·6 *	6·7	4·9
40	35·5	11·3 †	4	7·3
60	4·94	16·8	0·8	16·0

* 100 at 25°. † 74 at 25°.

TABLE 6

Rate constants in $HClO_4$ solutions in 40 vol. % dioxan–60% water mixtures at 1·1°

$HClO_4$ molarity	% R_3C^+ at equilibrium	k (sec.$^{-1}$)	k_{f} (sec.$^{-1}$)	k_{b} (sec.$^{-1}$)
0·105	3·0	7·1	0·2	6·9
0·209	7·6	5·6	0·4	5·2
0·314	18·1	5·0	0·9	4·1
0·419	35·3	5·6	2·0	3·6
0·523 *	46·4	6·5	3·2	3·3
0·733	73·3	9·6	7·1	2·5
1·047	92·0	28	26	2

* At 0·523M, k (sec.$^{-1}$) was 10·9 at 8·9°, 27 at 16·9° and 39 at 25·0°.

TABLE 7

Rate constants in $HClO_4$ solutions in 60 vol. % dioxan–40% water at 1·1°

$HClO_4$ molarity	% R_3C^+ at equilibrium	k (sec.$^{-1}$)	k_{f} (sec.$^{-1}$)	k_{b} (sec.$^{-1}$)
0·100	0·7	25·2	0·2	25
0·301	6·1	23·2	1·3	22
0·500 †	21·3	13·6	2·9	10·7
0·749	55·6	13·4	7·4	6·0
0·800	62·5	9·2	5·8	3·4
0·800	62·5	10·1 *	6·3	3·8
1·000	84·7	16·7	14·2	2·5
1·301	97	70	68	2
1·635	>98	89	88	1

* Disappearance of carbonium ion followed. † At 0·5M, k (sec.$^{-1}$) was 14·4 at 8·9°, 30 at 16·9°, and 44 at 25·0°.

At a fixed dioxan–water composition (Tables 6 and 7), the measured rate constant k passes through a minimum as the $HClO_4$ concentration is increased, due to the combination of a progressive, very marked, increase in k_{f} with a less marked decrease in k_{b}. This same decrease appeared in a few measurements in 40 vol. % dioxan on the dimethoxy-compound, 4,4′-dimethoxytriphenylmethanol, at 1·1° (with $pK_{\mathrm{R}} = -1·20$ at this temperature[14]) but in conditions in which the final carbonium ion concentration was negligibly small at equilibrium: at $HClO_4$ molarities of 0·523, 0·733, and 1·047, the k (and hence k_{b}) values were 49, 39, and 35 sec.$^{-1}$, respectively.

As the above H_{R} discussion implies, however, progressive increases in $HClO_4$ concentration in a mixed solvent produce systems which are very complicated from a kinetic point of view, and we therefore draw attention to Table 8, which summarises the results obtained when the overall perchlorate ion concentration was kept constant. At 0·5M, the qualitative features encountered in solutions of $HClO_4$ alone still appear, though to a less marked degree; but the results at 1·0M are of special interest, since they refer to conditions (20—85% conversion to the carbonium ion at equilibrium) which are particularly reliable for the sepration of k into k_{f} and k_{b}. From 0·086 to 1·0M-$HClO_4$ k_{b} now changes very much less than in the last column of Table 7, whilst k_{f} is almost proportional to the acid concentration (last column of Table 8). This confirms what would be expected from equation (1) that, under constant water activity and solvation conditions, only the forward reaction depends upon the acidity, the rate constant being proportional to the acid concentration.

TABLE 8

Rate constants in $LiClO_4$–$HClO_4$ solutions of constant perchlorate molarity in 60 vol. % dioxan at 1·1°

Total molarity	$HClO_4$ molarity	% R_3C^+ at equilibrium	k (sec.$^{-1}$)	k_{f} (sec.$^{-1}$)	k_{b} (sec.$^{-1}$)	$k_{\mathrm{f}}/[HClO_4]$ (l. mole^{-1} sec.$^{-1}$)
1·00	0·086	22·7	5·1	1·1	4·0	12·8
1·00	0·458	64·4	9·3 *	6·0	3·3	13·1
1·00	0·820	80·0	12·0	9·6	2·4	11·7
1·00	1·000	84·7	16·7	14·2	2·5	14·2
0·5	0·030	2·3	23	0·4	23	13·3
0·5	0·106	3·9	12·7	0·7	12	6·6
0·5	0·377	14·5	9·2 †	1·4	7·8	3·7
0·5	0·500	22·0	13·6	2·9	10·7	5·8

* 23 at 12·8°, 62 at 25·2°. † 23 at 12·8°, 41 at 25·1°.

EXPERIMENTAL

Equilibrium spectrophotometric measurements were made on a Unicam SP 600 spectrophotometer, with 4 cm. glass or 1 cm. quartz (stoppered) cells in a thermostatted metal support. The technique was similar to that of Dahn, Loewe, and Rotzler.[13]

The Gibson stopped-flow apparatus used for the kinetic experiments was set up in this laboratory by Professor R. G. Wilkins and has been described elsewhere.[20,21] Water thermostatted to 0·1° was circulated round the observation chamber. All experiments were carried out under first-order conditions and, despite the reproducibility of ±5% often obtained, the rate constants are probably only reliable to 12—15% for $k < 20$ sec.$^{-1}$ and become progressively less reliable at faster rates. Mr. L. N. Milnes of the Biochemistry Department, Sheffield University, kindly supplied two acid-resisting Kel-F mixers which were incorporated into the old apparatus. In a test, the rate constant for the formation of the blue peroxychromic acid from potassium dichromate and hydrogen peroxide was found to be 2·0 × 10^4 mole^2 l.$^{-2}$ sec.$^{-1}$ at 25°, in good agreement with the value recorded previously.[22]

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Acid of twice the required strength was generally placed in one of the syringes and a solution of the triaryl methanol of 10^{-4} to 10^{-6}M in the other, both being in the same solvent mixture. The monochromator (from a Unicam SP 500 spectrophotometer [20]) was set at the maximum absorption of the 4,4′,4″-trimethoxytriphenylcarbonium ion, which shifted slightly from 483 mμ in water to 490 mμ in dioxan for HCl solutions: in the 40 and 60 vol. % dioxan solutions it was at 486 mμ in perchloric acid. (The extinction coefficient also increased steadily from $8{\cdot}78 \times 10^4$ to $10{\cdot}45 \times 10^4$ at 25° on changing from water to dioxan–HCl solutions, always increased a few percent on lowering the temperature, and was lower for $HClO_4$ than for HCl solutions.)

1,4-Dioxan was purified as described by Vogel [23] and was always used promptly after purification. A stock 5·4M-HCl solution in anhydrous dioxan was obtained by passing the gas, after drying with 98% H_2SO_4, into the anhydrous solvent. 2M-Stock solutions of HCl in aqueous dioxan solutions were made up as described by Braude and Stern,[16] and all acids were standardised with NaOH.

An *x* vol. % dioxan mixture here signifies that *x* ml. of pure dioxan was mixed with sufficient of an aqueous solution of any necessary additives (acid or indicator) to give the required final concentrations, plus enough water to make up to 100 ml. Made up in this way,[16] 20, 40, 60, 70, 80, 90, and 95 vol. % dioxan correspond, respectively, to 5·0, 12·3, 24·0, 33·0, 45·7, 65·2, and 80·0 mole % dioxan.

Perchloric acid solutions were made from standardised 72% $HClO_4$, the dioxan : water volume ratio being obtained by keeping the weights at 414·12 g. dioxan to 598·92 g. water (for 40 : 60) and 621·18 g. dioxan to 399·28 g. water (for 60 : 40). $LiClO_4$ Solutions were always made from the acid and weighed quantities of B.D.H. reagent grade Li_2CO_3.

4,4′,4″-Trimethoxytriphenylmethanol was prepared from *p*-methoxyphenylmagnesium bromide and methyl anisate.[12,13,24] The reactants were refluxed in dry ether overnight, after which dry benzene was added, the ether distilled off, and the solution refluxed for 30 min. After cooling, the magnesium complex was destroyed by aqueous NH_4Cl and the product was extracted into benzene. The red gum obtained after removal of the benzene was purified by t.l.c. on silica gel. Recrystallisation from aqueous ethanol yielded colourless crystals, m. p. 81—82° (lit.,[25] 83·5—84°). Since it proved somewhat unstable, the compound was purified immediately before use.

4,4′-Dimethoxytriphenylmethanol was prepared similarly from *p*-methoxyphenylmagnesium bromide and methyl benzoate, but the gum was used directly in this case as it could not be induced to crystallise. The absence of ester and carbonyl groups was established spectroscopically.[13]

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