Solvent Effects on the Rates of Some Acid-catalysed Reactions

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Rate constants for some acid-catalysed reactions are reported together with H_0 acidity functions in dilute solutions of perchloric acid in dioxan–water mixtures at various temperatures. Rate constants in dioxan–water mixtures containing 0·1M-hydrochloric acid are also reported. In all cases graphs of log (observed rate constant) against H_0 are linear for reactions in perchloric acid solutions of fixed solvent composition. The slopes of these graphs are relatively insensitive to solvent composition except for the A-2 reactions studied, for which the slopes show an appreciable solvent-dependence. The effects of changing solvent composition on the reaction rates in solvents containing a constant concentration of mineral acid catalyst are compared by plotting graphs of H_0 + log k against log (activity of water). With 0·1M-perchloric acid catalyst approximately linear correlations are obtained which are discussed in terms of the reaction mechanism. Comparison of results obtained with perchloric and hydrochloric acid catalyst also throws light on the reaction mechanisms.

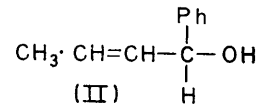
For the hydrolysis of ω-diazoacetophenones in aqueous dioxan containing 0·1M-perchloric acid, graphs of H_0 + log k against percentage of water in the solvent are approximately linear, with negative slopes.[1] This result is qualitatively in agreement with Bunnett's treatment [2] for an A-1 reaction. Although the mechanism of ω-diazoacetophenone hydrolysis had not been firmly established the result suggested that such correlations might be used for diagnostic purposes. Solvent effects were therefore studied by use of the following compounds: ethyl diazoacetate (I), 1-phenylbut-2-en-1-ol (II), α-diazodeoxybenzoin (III), 9-diazofluorene (IV), 3-diazo-1-methoxycarbonyloxy-1-phenylacetone (V), ω-diazoacetophenone (VI), and diazo-(4-methylphenylsulphonyl)-methane (VII).

The reactions were chosen to provide examples of different acid-catalysed mechanisms. The hydrolysis of the ester (I) [3] is a well established example of the A-2 mechanism. The rearrangement of the butene (II) [4] involves intra- and/or inter-molecular participation of water in the rate-determining step. Hydrolyses of the ketone (III) [5,6] and the fluorene (IV) [6,7] are well established examples of the A–S_E2 mechanism. A-1 and A-2 routes have both been suggested [8,9] for the hydrolysis of ketones (V) and (VI). In the presence of hydrochloric acid the sulphonyl compound (VII) [10] seems to hydrolyse by the A-2 route although in perchloric acid the Bunnett w-value (—2·3) is consistent [2] with the A-1 route for an oxygen or nitrogen base.

The chosen substrates give fairly convenient rates in 0·1M-perchloric acid solutions at readily accessible temperatures. Interpretation of the results is thus simplified because the ionic strength is constant and only one indicator is needed to measure H_0.

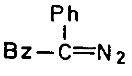
$N_2CH{\cdot}CO_2Et$

(I)



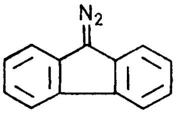
$CH_3{\cdot}CH{=}CH{-}C(Ph)(H){-}OH$

(II)

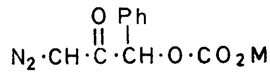


$Bz{-}C(Ph){=}N_2$

(III)

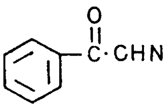


(IV)

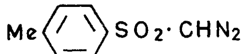


$N_2{\cdot}CH{\cdot}C(=O){\cdot}CH(Ph){\cdot}O{\cdot}CO_2Me$

(V)



(VI)



(VII)

Before the effects of changing solvent composition were investigated the suitability of the indicator was checked by studying the correlation between H_0 and log k in different solvent mixtures containing perchloric acid.

It was considered of interest to compare solvent effects in solutions of 0·1M-perchloric and 0·1M-hydrochloric

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[2] J. F. Bunnett, *J. Amer. Chem. Soc.*, 1961, **83**, 4956 *et seq.*

[3] (*a*) W. J. Albery and R. P. Bell, *Trans. Faraday Soc.*, 1961, **57**, 1942; (*b*) W. J. Albery and M. H. Davies, *ibid.*, 1969, **65**, 1066; (*c*) W. J. Albery, J. E. C. Hutchins, R. M. Hyde, and R. H. Johnson, *J. Chem. Soc.* (*B*), 1968, 219.

[4] (*a*) E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1948, 1982; (*b*) E. A. Braude, *Ann. Reports*, 1949, **46**, 125; (*c*) E. A. Braude, *Quart. Rev.*, 1950, **4**, 404.

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[8] H. Dahn and H. Gold, *Helv. Chim. Acta*, 1963, **46**, 983.

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acids since the mechanisms may be affected by the nucleophilicity of the anion.

EXPERIMENTAL

Materials.—Ethyl diazoacetate [11] and 1-phenylbut-2-en-1-ol [12] were prepared by standard methods and purified by distillation at reduced pressure. α-Diazodeoxybenzoin, m.p. 79 °C (from ether) (lit.,[13] 79 °C), and 9-diazofluorene, m.p. 98·4 °C (lit.,[13] 94—95 °C) from light petroleum (b.p. 30—40 °C), were prepared by oxidation of the corresponding hydrazones.[13] 3-Diazo-1-methoxycarbonyloxy-1-phenylacetone, m.p. 110·5 °C (lit,[8] 111 °C), from light petroleum (b.p. 60—80 °C)–methanol, was prepared as described by Dahn and Gold.[8] ω-Diazoacetophenone was prepared and purified as described.[14] Diazo-(4-methylphenylsulphonyl)-methane, m.p. 34—36 °C from ether (lit.,[15] 34—37 °C), was prepared by the method of van Leusen and Strating.[15] The purification of dioxan and *m*-nitroaniline have been described.[1] Perchloric and hydrochloric acid stock solutions were prepared by diluting AnalaR acids with distilled water and standardised by titration.

TABLE 1

H_0 Acidity functions for perchloric acid in 50 and 90% dioxan–water mixtures at different temperatures

$[HClO_4]$/	50% Dioxan–water			90% Dioxan–water		
M	10 °C	15 °C	25 °C *	15 °C	25 °C	35 °C
0·010	3·05	3·12	3·21	3·29	3·30	
0·020	2·82	2·83	2·87	2·96	3·00	
0·030	2·58	2·61	2·72	2·79	2·82	
0·050	2·31	2·38	2·46	2·55	2·56	2·54
0·080		2·15	2·22	2·27	2·29	2·29
0·100	1·87	2·02	2·11	2·13	2·15	2·13
0·160					1·85	1·81
0·200			1·74		1·65	1·67

* From ref. 1.

TABLE 2

Rate constants (10^2k/min^{-1}) in 50 and 90% dioxan–water mixtures containing $HClO_4$

	50% Dioxan–water					90% Dioxan–water						
	(I) 24·95 °C	(II) 29·79 °C	(III) 24·95 °C	(IV) 14·50 °C	(VII) 29·79 °C	(I) 24·95 °C	(II) 29·79 °C	(III) 24·95 °C	(IV) 14·50 °C	(V) 35·00 °C	(VI) 24·95 °C	(VII) 29·79 °C
0·010	3·43	3·26		3·95		2·17	1·69		1·47			
0·020	6·93	5·78	1·04	8·30		4·50	3·49		2·99			
0·030	11·3	8·99		13·7		7·40	5·69	0·550	4·45		0·808	0·219
0·050	19·6	14·5	2·21	25·2	0·197	14·1	11·1	0·887	8·01	0·110	1·42	0·427
0·080	35·4	24·7	3·49	41·9	0·303	26·4	19·7	1·64	14·6	0·199	2·71	0·804
0·100	43·7	41·4	4·27	59·6	0·423	42·3	28·9	2·21	20·9	0·293 *	3·64 *†	1·05
0·140					0·682							
0·150			6·85					3·81				
0·160										0·625	8·19	2·11
0·170					0·738							
0·200			9·25		0·970			5·74		0·833	13·2	3·22

* Determined by nitrogen evolution. † From ref. 1.

TABLE 3

Acidity functions in dioxan–water mixtures containing 0·100M-perchloric acid

	H_0	
Volume % dioxan	15 °C	35 °C
40	1·81	1·87
50	2·02	2·08
60	2·24	2·36
70	2·39	2·50
80	2·43	2·46
90	2·13	2·13

Methods.—Acidity functions were measured in the usual way [16] with a Unicam SP 500 spectrophotometer. *m*-Nitroaniline, for which [17] pK_a was taken to be 2·50, was used as indicator.

Reaction rates were measured by the nitrogen evolution method [14] or spectrophotometrically by following the decrease or increase of a characteristic absorption of the substrate or product. The following wavelengths were used: (I), 250 nm (decrease); (II), 250 nm (increase); (III), 325 nm (decrease); (IV), 350 nm (decrease); (V), 252 nm (decrease); (VI), 295 nm (decrease); (VII), 252 nm (decrease). The general procedure for spectrophotometric rate measurements was as follows. A stock solution of the substrate in dioxan was mixed with appropriate amounts of water and dioxan and the mixture equilibrated in a thermostat bath. The reaction was started by adding the necessary volume of a stock solution of acid, and the mixture transferred to a 1 cm stoppered cell in the thermostatically controlled cell housing of a Unicam SP 500 spectrophotometer. The temperature in the cell housing was measured by use of a thermistor placed in a cell; temperature control in the cell was to ±0·03 °C. The output of the instrument was continuously recorded on a Rikadenki recorder type B24. Rate constants were calculated by use of the integrated first-order equation or Guggenheim's method.[18] The reproducibility of the rate constants was ±3%.

The meaning of *x*% (v/v) of dioxan has been described.[1]

H_0 Acidity functions and observed rate constants, *k*, in 50 and 90% solutions of perchloric acid are shown in Tables 1 and 2. Table 1 includes values of H_0 at 25 °C for comparison. Table 3 lists acidity functions in 0·1M-perchloric acid solution. Table 4 shows rate constants in 0·1M-perchloric and 0·1M-hydrochloric acids in different dioxan–water mixtures. Except where otherwise indicated rate constants were determined spectrophotometrically.

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[12] H. Burton, *J. Chem. Soc.*, 1929, 455.

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DISCUSSION

Acidity Functions.—Table 1 shows that H_0 increases slightly with increasing temperature in 50% dioxan–water mixture between 10 and 25 °C, but the change of H_0 with temperature is insignificant in 90% dioxan–water between 15 and 35 °C. In 0·1M-perchloric acid solutions $-H_0$ passes through a minimum as the proportion of dioxan in the mixture changes from 40 to 90% (Table 3). The position of the minimum is unaffected by temperature between 15 and 35 °C but the temperature-dependence of H_0 seems to be greatest near the minimum.

TABLE 4

Rate constants (10^2k/min^{-1}) in dioxan–water mixtures containing 0·100M-acid

Volume % dioxan	(I)		(II)	(III)		(IV)		(V)		(VI)	(VII)	
	24·95 °C		29·79 °C	24·95 °C		14·50 °C		35·00 °C		24·95 °C	29·79 °C	
	$HClO_4$	HCl	$HClO_4$	$HClO_4$ *	HCl	$HClO_4$	HCl	$HClO_4$	HCl	HCl	$HClO_4$	HCl
40	76·2	148			5·15	122		0·140	0·445	4·25	0·697	0·888
45			60·7				70·0					
46				6·83								
50	43·7	108	41·4	5·37	3·69	59·6	47·3	0·107	0·405	3·75	0·423	0·630
60	25·6	72·9	24·0		2·75	27·9	24·4	0·0847	0·414	3·42	0·276	0·540
68				2·05								
70	19·1	75·5	17·4		2·73	16·1	16·6	0·0792	0·573	4·16	0·222	0·582
76				1·70								
80	18·4	102	16·3		6·82	12·2	22·5	0·130	1·06	7·56	0·270	0·990
83				1·79								
85			20·3		13·5	13·6	69·2					
90	42·3	132	28·9	2·62		20·9	104	0·293	2·60	22·8	1·05	3·04
92				3·62								
95						60·4						

* Determined by nitrogen evolution.

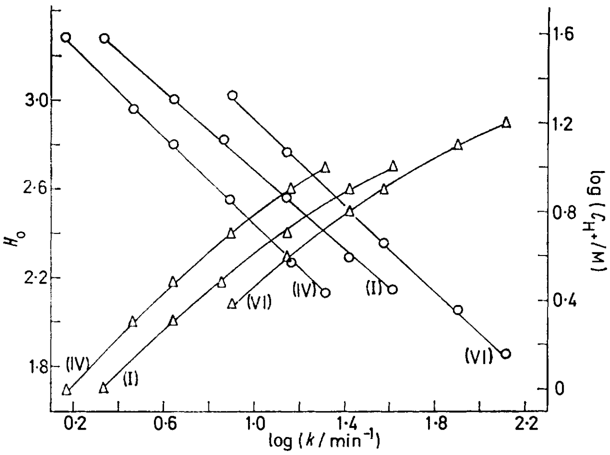


FIGURE 1 Typical H_0–log k (○) and log C_{H^+} − log k (△) graphs for results in 90% dioxan–water. For (I) and (IV), 2 has been added to log k and log C_{H^+}. For (VI), 3 has been added to log k, 0·2 to H_0, and −0·1 to log C_{H^+}

log k–H_0 Relationships.—For results in 50 and 90% dioxan–water mixtures graphs of log k against H_0 are good straight lines for all the substrates studied. In terms of linearity there is little to choose between graphs of log k against H_0, and log k against log C_{H^+}, when the results for 50% dioxan solutions are used. There is a clear distinction when the results for 90% dioxan mixtures are used: graphs of log k against H_0 are linear whereas graphs of log k against log C_{H^+} are curved (see Figure 1). Slopes of graphs of log k against H_0 are collected, together with values reported by other workers, in Table 5. The values for the sulphonyl compound (VII) compare with values of −1·15 and −1·12 reported[10] for diazo-(4-nitro- and -(4-methoxy-phenylsulphonyl)methane in 40% dioxan–water solutions of perchloric acid at 25 °C. Zucker–Hammett slopes of −1·01 (50% dioxan–water),[1] −1·04 (60% dioxan–water),[8] and −1·13 (water) [9] have been reported for ω-diazo-4′-methoxy-, -4′-nitro-, and -3′-fluoro-acetophenone respectively at 25 °C in perchloric acid solutions. Some of the Zucker–Hammett slopes reported by other workers for the same or similar substrates are appreciably higher than ours. In every case the higher values were obtained with very much higher concentrations of acid catalyst and may well be due to a positive, primary salt effect. The slopes of log k–H_0 graphs are relatively insensitive to solvent composition except for the two reactions in which water is involved in the rate-determining step. In these cases the magnitude of the slopes increases by *ca*. 15% in changing from 50 to 90% dioxan.

TABLE 5

Slopes of graphs of log k against H_0 in different water–dioxan mixtures

Substrate	Volume % dioxan: 0	40	50	60	90
(I)	−1·07 (0 °C) [a]		−1·00 (25 °C)		−1·14 (25 °C)
(II)			−0·91 (30 °C)		−1·06 (30 °C)
(III)		−0·9 (25 °C) [b]	−0·86 (25 °C)		−0·88 (25 °C)
(IV)			−1·05 (15 °C)		−0·99 (15 °C)
(V)		−1·10 (25 °C) [c,d]		−1·02 (25 °C)	−1·01 (35) °C
(VI)			−1·00 (25 °C) [e]		−1·03 (25 °C)
(VII)			−0·98 (30 °C)		−0·99 (30 °C)

[a] Ref. 3(*a*). [b] Ref. 5. [c] Ref. 8. [d] Ref. 9. [e] Ref. 1.

Effect of Solvent Composition.—One method of treating solvation effects on the rates of acid-catalysed reactions is due to Bunnett,[2] who derived the relationship (1) between H_0, k, and water activity a_w in the case of a weakly basic substrate. In this equation, t, s, a, and b

$$H_0 + \log k = \text{constant} + [(t - s) - (a - b)] \log a_w \quad (1)$$

represent the numbers of molecules of water of solvation associated with the transition state, the initial solvated state, the indicator conjugate acid, and the indicator base, respectively. The equation was derived for aqueous solutions but should hold in dioxan–water mixtures provided that dielectric constant effects are negligible and that differential solvation by dioxan is neglected. Bunnett's assumption that activity coefficient ratios for species of like charge are independent of solvent composition must also be valid.

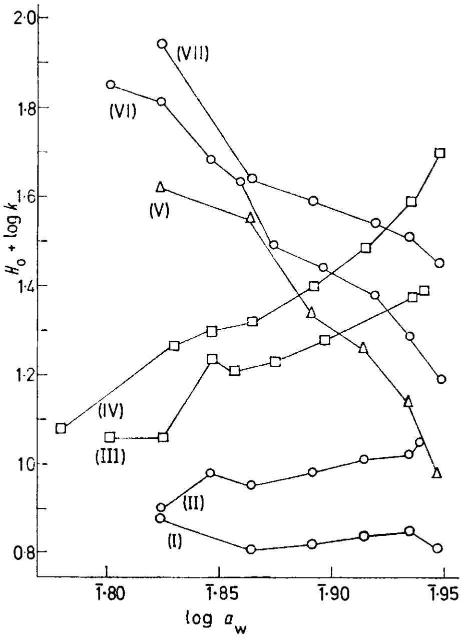


FIGURE 2 $H_0 + \log k$ as a function of log a_w for the hydrolyses of compounds (I)—(VII) in dioxan–water mixtures containing 0·100M-HClO$_4$. Data for (VI) were taken from ref. 1. Arbitrary constants x have been added to $H_0 + \log k$ as follows: (I), $x = -0·9$; (II), $x = -0·7$; (III), $x = 0·55$; (IV), $x = -0·2$; (V) $x = -2·0$; (VI), $x = 1·1$; (VII), $x = 1·79$

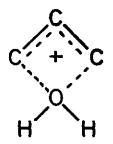
From considerations of dielectric constant alone the left-hand side of equation (1), which corresponds approximately to the logarithm of the rate constant at zero H_0, would be expected[19] to decrease with the proportion of water in the solvent for A-2 and A–S_E2 reactions. This is not the case for perchloric acid solutions; further, overall changes in $H_0 + \log k$ are much larger than would be expected from dielectric constant effects in most cases.[19] It appears therefore that dielectric constant effects are of minor importance and that solvation effects are the predominant factor in determining changes in $H_0 + \log k$ in perchloric acid solutions.

This is in agreement with the comments of Cox and McTigue[20] with regard to solvent effects on unimolecular and ion–dipole reactions.

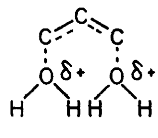
When a single indicator is used to measure H_0 the relative slopes of the Bunnett plots for different substrates are given by the relative values of $(t - s)$ since the contribution of $(a - b)$ to the slopes is constant. Thus the expected order of the Bunnett slopes is A–S_E2 > A-2 > A-1 when the same indicator is used throughout.

Figure 2 shows $H_0 + \log k$ in 0·1M-perchloric acid solutions plotted against log a_w for compounds (I)—(VII). In the absence of data for solutions containing 0·1M-perchloric acid values of a_w in binary dioxan–water mixtures[21] were used. It is reasonable to expect that changes in a_w in dilute solutions of perchloric acid are proportional to changes in a_w in the solvent. The reactions all give approximately linear correlation curves and fall clearly into three groups in Figure 2. As expected, the two A–S_E2 reactions give lines with more positive slopes than do the two reactions in which water is involved in the rate-determining step. The slopes for the fluorene (VI) (*ca.* +4) and the butene (II) (*ca.* +1·3) are in the ranges predicted by Bunnett[2] for an A–S_E2 and A-2 reaction respectively. The slopes for the benzoyl derivative (III) (*ca.* +2·5) and the ester (I) (*ca.* −0·6) are *ca.* 0·5—3 units more negative than predicted for purely aqueous solutions.

An intra- and/or inter-molecular mechanism for the rearrangement of the butene (II) has been suggested[4] which proceeds *via* a cyclic four-membered transition state (A) or acyclic transition state (B). It was suggested that the mechanism must be intramolecular in anhydrous dioxan but transition state (B) may also be involved in aqueous dioxan. The similarity of lines for compounds (I) and (II) in Figure 2 suggests that the intermolecular A-2 mechanism is favoured in aqueous dioxan.



(A)



(B)

Compounds (V)—(VII) give lines with approximately the same slope of between −4 and −5. An obvious conclusion to be drawn from Figure 2 is that these three substrates hydrolyse by the same mechanism which is neither A–S_E2 nor A-2 involving oxygen or nitrogen protonation. The negative slopes of the lines for (V)—(VII) are consistent with either of the likely possibilities: an A-2 mechanism with carbon protonation or an A-1 mechanism with oxygen or nitrogen protonation. I.r. spectra,[22] EHMO calculations,[23] n.m.r. spectra in superacid solutions,[24] and a consideration[25] of the relative

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rates of protonation at carbon and oxygen all indicate that the most likely site of protonation for primary diazoketones is the keto-oxygen atom. It is therefore concluded that compounds (V)—(VII) hydrolyse by *A*-1 mechanisms in the presence of perchloric acid.

Figure 3 shows $H_0 + \log k$ plotted against $\log a_w$ when 0·1M-hydrochloric acid is used as catalyst. H_0 Values due to Braude and Stern [26] were used with the addition of 0·07, the difference between the pK_a value used in this work and that used by Braude and Stern. The use of a_w values valid in binary mixtures is probably less justifiable in this case than in the case of 0·1M-perchloric acid because of the greater salting-out effect of the chloride ion than of perchlorate ion; the effect may vary with solvent composition. There are some interesting differences between Figures 2 and 3. Compounds (I), (V), (VI), and (VII) give similar results in hydrochloric acid. The overall changes in $H_0 + \log k$ for compounds (V), (VI), and (VII) in hydrochloric acid solutions are about twice those obtained in perchloric acid solutions, the enhancement being greater in solutions with lower water content (see Figure 4). A study of the enhancement by chloride ion of the rate of hydrolysis of compounds (I),[3a] (V),[9] and (VII) [10] provided evidence for the suggested *A*-2 mechanism for the hydrolysis of these substrates. However, clear evidence for an *A*-2 mechanism in the presence of perchloric acid alone has only been obtained in the case of the ester (I).[3b,c] The effect of chloride ion on the hydrolysis of the ketone (VI) has not been studied systematically but in the reaction in aqueous buffers containing chloride ion some chloro-product is formed.[27] The difference in behaviour of (I) and that of (V)—(VII) in perchloric acid compared with the similarity of their behaviour in hydrochloric acid strongly supports the suggestions [8,28] that the mechanism of primary diazoketone and diazosulphone hydrolyses may change from *A*-1 in the presence of perchlorate ion to *A*-2 in the presence of the more strongly nucleophilic chloride ion. The greater rate enhancement in solutions with lower water content is as expected [19] on the basis of dielectric constant effects for a reaction between oppositely charged ions.

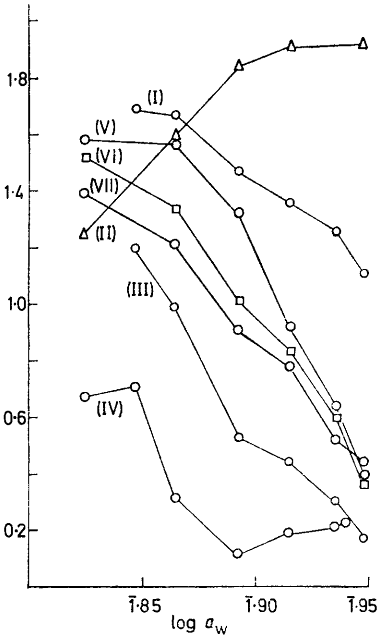

FIGURE 3 $H_0 + \log k$ as a function of $\log a_w$ for the hydrolyses of compounds (I)—(VII) in dioxan–water mixtures containing 0·100M-HCl. Data for (II) were taken from ref. 4*a*, H_0 values from ref. 26 (but see text). Arbitrary constants x have been added to $H_0 + \log k$ as follows: (I), $x = 1{\cdot}2$; (II), $x = 0{\cdot}3$; (III), $x = -0{\cdot}3$; (IV), $x = -1{\cdot}5$; (V), $x = 1{\cdot}0$; (VI), $x = 0$; (VII), $x = 0{\cdot}75$

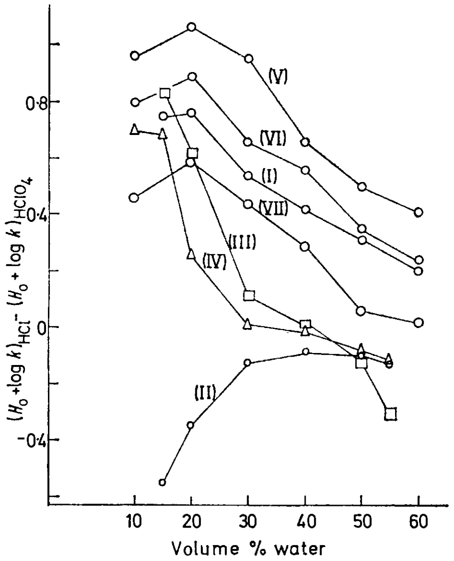

FIGURE 4 $(H_0 + \log k)_{HCl} - (H_0 + \log k)_{HClO_4}$ for compounds (I)—(VII) as a function of solvent composition

There is a fairly well defined change in the slope of the lines for compounds (III) and (IV) at about 30% (v/v) of water ($\log a_w = ca.\ 0{\cdot}89$) in the presence of hydrochloric acid. Below 30% (v/v) of water the slope is much more negative than it is above it. Also with both substrates the corrected rates are increased by changing from perchloric to hydrochloric acid below 30—40% water, and decreased at higher water contents (see Figure 4). In both particulars (slope of the correlation curve and rate enhancement by chloride ion) in solvents containing less than 30% water, the reactions of compounds (III) and (IV) behave like those in which chloride is involved in the rate-determining step. It is possible that (III) and (IV) hydrolyse by an *A*-2 mechanism, or concurrent *A*–S_E2 and *A*-2 mechanisms, in these mixtures in the presence of hydrochloric acid.

The lower values of $H_0 + \log k$ with hydrochloric acid than with perchloric acid for compounds (III) and (IV) in solvents containing more than 30% water can be accounted for by considering the greater structure-breaking effect of chloride than of perchlorate ion (this is well illustrated by the solubility gap observed [26] in

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[26] E. A. Braude and E. S. Stern, *J. Chem. Soc.*, 1948, 1976.

[27] M. Bailes and L. L. Leveson, *J. Chem. Soc.* (*B*), 1970, 34.

[28] C. W. Thomas and L. L. Leveson, *J. Chem. Soc.* (*B*), 1970, 1061.

dioxan–water mixtures containing 1M-hydrochloric acid; no such gap occurs with 1M-perchloric acid). Less water is available for stabilisation of the transition state by solvation, and the rate of reaction is decreased when perchlorate is replaced by chloride ion. Thus protonation may persist as the rate-determining step in solvents containing more than 30% water.

The rearrangement of the butene (II) is the only reaction of those studied whose rate is decreased in all solvent mixtures by the change from perchloric to hydrochloric acid (Figure 4). This is consistent with the structure-breaking effect of chloride ion and the known inability of chloride ion to participate as a nucleophile in the rate-determining step in this reaction,[4] which also accounts for the difference in behaviour of this substrate and (I) in hydrochloric acid solutions. With compound (II) as with (III) and (IV) there is a change in the slope of the correlation curve in Figure 3 at *ca.* 30% water; this is approximately the point at which the minimum occurs in the acidity-function curve and may be the composition at which a significant change occurs in the solvent structure. The larger inhibiting effect of the chloride ion in solvents containing less than 30% water may simply reflect its greater structure-breaking effect in solvents with low water contents (with 1M-hydrochloric acid miscibility is incomplete when less than *ca.* 20% of water is present). However it is possible that the change in slope is associated with a change from largely intermolecular involvement of water in the rate-determining step to largely intramolecular involvement as the proportion of water in the solvent decreases.

We thank Mr. P. A. Smith for preparing the sample of diazo-(4-methylphenylsulphonyl)methane and for some kinetic measurements with it.

[2/1272 *Received, 5th June,* 1972]