General Acid Inhibition and the Absence of Deuterium Isotope Exchange in Base Catalysed Hydrolysis of 2,4-Dinitrophenyl Arylmethanesulphonate Esters in Aqueous Solution

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The hydrolysis of 2,4-dinitrophenyl arylmethanesulphonates in aqueous buffers exhibits general base catalysis at low buffer concentration. The rate constant–buffer concentration plots become non-linear at high concentrations and this is interpreted as due to a change in rate-limiting step from proton transfer to the breakdown of the sulphene–2,4-dinitrophenolate ion encounter complex. Experiments with added solutes and kinetic arguments indicate that the curvature in the buffer concentration plots is not due to specific solute effects. The absence of deuterium exchange at high buffer concentration is consistent with an internal return mechanism which is more efficient than exchange processes; a water molecule is proposed to act as a relay for the transfer of proton from carbon acid to base.

RECENT work from King's [1] and our laboratories [2] indicates that the decomposition of aryl phenylmethanesulphonate esters is general base catalysed for weakly basic leaving groups. At higher basicities ($pK_a^{ArOH} > 7$) a change in rate-limiting step occurs, the detail of the mechanism alters from $E1cB_i$ to $E1cB_r$ and only specific base catalysis is observed. As the basicity of the leaving aryl oxide ion decreases the carbanionic intermediate in the $E1cB_i$ mechanism becomes too unstable to exist as a

$$PhCH_2SO_2OAr \overset{B}{\rightleftharpoons} PhC\bar{H}SO_2\text{–}OAr \longrightarrow PhCH{=}SO_2 + \bar{O}Ar \quad (1)$$

discrete intermediate and the reaction then involves an $E2$ decomposition of ester by base to yield sulphene [equation (1)] which is trapped by nucleophile to yield products. Previous work [2b,c] provides estimates of the half-life of the carbanion in equation (1) and indicates a value of $<10^{-13}$ s for leaving phenols with $pK_a < 6$; these carbanions cannot exist as discrete species.[3] The $E2$ mechanism is proposed [2] to involve extensive C–H cleavage but little S–O fission in the transition state and may be termed a paenecarbanion mechanism. For esters of phenols with pK_a values <6 it is expected that increase in the general acid concentration would not be sufficient to cause a changeover from the $E1cB_i$ to the $E1cB_r$ mechanism; we therefore would expect no curvature in the plots of rate constant *versus* buffer concentration for these esters.

This work extends and confirms the observations reported in a previous communication [4b] that buffer curvature exists in the plots of rate constant *versus* concentration for 2,4-dinitrophenyl esters of arylmethanesulphonic acid. We examine all the simple possibilities which could give rise to buffer curvature and are led to the conclusion that the observation is due to a change in rate-limiting step; proton transfer in an encounter complex is rate limiting at low buffer concentration while at high buffer concentration it is decomposition of the sulphene–aryl oxide encounter complex. Isotope studies using deuterium oxide solvent show the absence of exchange reminiscent of previous results for elimination reactions.[5] We believe these observations indicate an extensive 'internal return' mechanism.

EXPERIMENTAL

Materials.—Substrates were prepared as described in the accompanying paper.[6] Materials such as buffers and reagents were obtained commercially and were of analytical grade or were recrystallised or redistilled before use. Deuterium oxide (99.7% D) and 35% DCl in D_2O (99% D) were obtained from Merck, Sharp and Dohme Ltd.

Methods.—Kinetics were determined as described in the following paper.[6] Deuterium exchange experiments were carried out as follows: a solution of 2,4-dinitrophenyl phenylmethanesulphonate (0.05M) and pyridine buffer (2M; fraction of base 0.5) in 70% (v/v) acetonitrile–D_2O was kept at 25°. The progress of the reaction was monitored by diluting a 10λ portion in 95% (v/v) ethanol–water (2.5 ml) and measuring the absorbance at 293 nm. The absorbance change in a preliminary experiment was from 0.53 to 1.38 units and the reaction was therefore quenched at 50% completion (*ca.* 80 min) when the absorbance reached 0.96 units. Quenching was accomplished by adding DCl dropwise to the solution cooled in an ice-bath till the yellow colour was discharged. The substrate was recovered by extraction with chloroform and recrystallised from ethyl acetate. The ^1H n.m.r. spectrum of the recovered substrate was measured using $CDCl_3$ solvent and a Varian FT80 instrument. Integration of the signals centred at δ 8.85 and 8.44 (aromatic) were compared with that δ 4.76 (benzylic CH_2).

Experiments involving product analysis for deuterium content from hydrolysis of 2,4-dinitrophenyl phenylmethanesulphonate in deuterium oxide buffers were carried out as follows. Ester in dimethoxyethane was added portionwise to the buffer containing 80% (v/v) 1,1-dimethoxyethane–pyridine (2M; fraction base 0.5; 25°). 1,1-Dimethoxyethane was present as co-solvent to solubilise relatively large concentrations of substrate. The product was acidified with DCl and extracted with dichloromethane; the 100 MHz n.m.r. spectrum of the aqueous solution was examined together with a control spectrum of natural sodium phenylmethanesulphonate. The n.m.r. machine

used in these experiments was a JEOL 100 MHz instrument and we are grateful to Dr. D. O. Smith for its operation.

RESULTS

The liberation of 2,4-dinitrophenol from the substrates in aqueous buffers obeyed good first-order kinetics over *ca.* 90% of the total reaction. The rate constants for cacodylate, *NN*-dimethylaminoacetonitrile, acetate, and *N*-propargylmorpholine buffers exhibited a non-linear dependence on

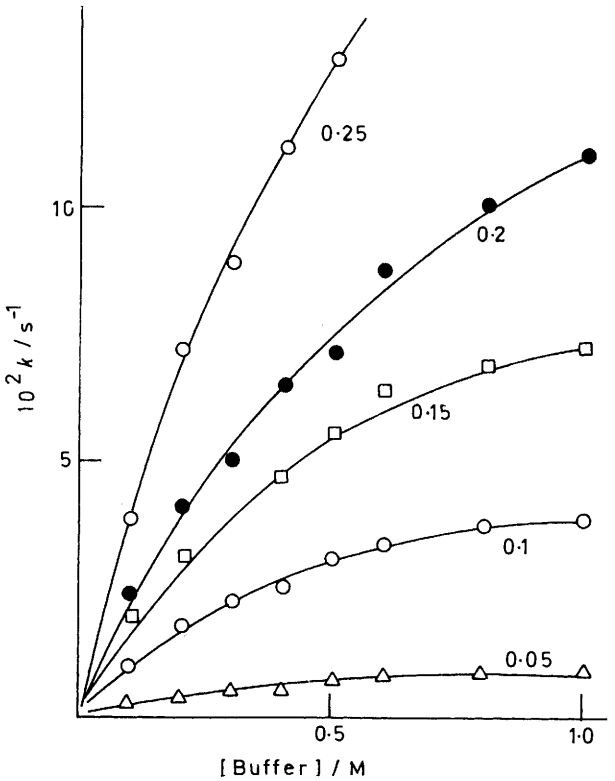


FIGURE 1 The reaction of 2,4-dinitrophenyl 4-chloro-2-nitrophenylmethanesulphonate in cacodylic acid buffers. Conditions as in Table 1; the lines are theoretical from parameters in Table 1 using equation (2)

the concentration of the buffer species; the rate constants fitted equation (2). The non-linear dependence is illustrated in Figure 1 for the cacodylate buffers reacting with 2,4-

$$k_{obs} = k_{max.}[B]/(K + [BH]) \qquad (2)$$

dinitrophenyl 4-chloro-2-nitrophenylmethanesulphonate. The data are collected in Table 1 and that for pyridine catalyst is reported in the following paper.[6]

The value of $k^{max.}$ is independent of the buffer species and proportional to hydroxide ion concentration (Figure 2).

Since the concentration of buffer over which curvature is observed is relatively high it is necessary to consider the possibility of specific solute and solvent effects as explanations rather than a more significant change in rate-limiting step. Experiments were therefore carried out on the decomposition of substrates in media of different composition; added *N*-methylpyridinium iodide, potassium iodide, pyrimidine, dioxan, ethanol, and indole showed some effect (Table 2) but this was smaller than that of the original non-linear buffer plots.

Deuterium exchange experiments indicated that no deuterium was incorporated into 2,4-dinitrophenyl phenylmethanesulphonate remaining after 50% had hydrolysed under conditions given in the methods where significant incorporation should be observed. This important finding

TABLE 1

Kinetic parameters for buffer catalysed hydrolysis of 2,4-dinitrophenyl arylmethanesulphonate esters [a]

F.B.[b]	N [c]	pH	pK_a	$10^{-2} k_{max.}$/s^{-1}	K/mol l^{-1}	$10\,k_{OH}^{max.}$/l mol^{-1} s^{-1} [d]
4-Chlorophenyl-2-nitro-methanesulphonate						
Cacodylate						
0.05	8	4.60	6.15	1.29	0.51	9.0
0.1	8	4.76		6.25	0.50	11
0.15	8	5.17		12.5	0.50	8.4
0.2	8	5.41		22.7	0.72	9.0
0.25	8	5.53		31	0.54	9.1
Pyridine						
0.05	7	4.46	5.30	2.57	0.37	8.1
Acetate						
0.3	7	4.04	4.51	1.25	0.90	11
0.5	7	4.51		2.66	0.71	8.2
3-Nitrophenylmethanesulphonate						
Pyridine						
0.5	8	5.3	5.3	4.28	0.56	1.4
0.2	11	4.95		1.29	0.56	1.5

[a] Conditions: 25 °C and 1M ionic strength made up with KCl. [b] Fraction of the base species. [c] Number of data points. [d] Using pK_w 13.97; the average value for $k_{OH}^{max.}$ is $9.2.10^7$ l mol^{-1} s^{-1} for the 4-chloro-2-nitro derivative.

was substantiated by measuring the rate constant for hydrolysis of the 2,4-dinitrophenyl phenylmethanesulphonate in pyridine buffer (2M; fraction base 0.5; 25°) using water and deuterium oxide. The resultant rate constants (1.32×10^{-3} and 1.27×10^{-3} s^{-1}) are identical within the experimental error. Plots of log $(A_t - A_\infty)$ *versus* time were perfectly linear over more than three half-lives and

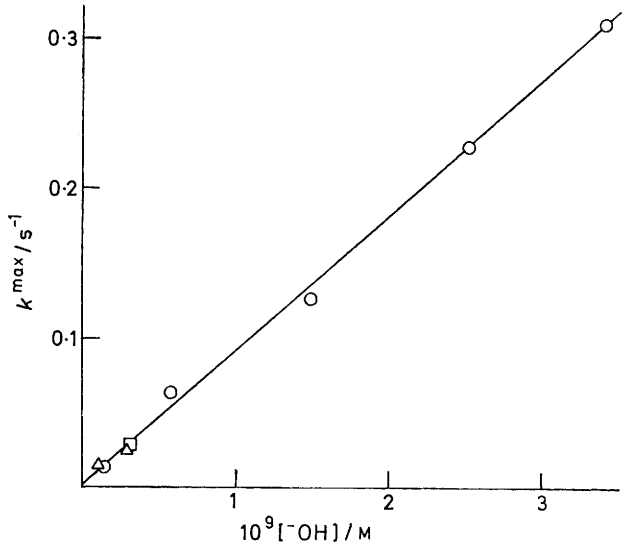


FIGURE 2 Dependence on hydroxide concentration of $k^{max.}$ for the reaction of 2,4-dinitrophenyl 4-chloro-2-nitrophenylmethanesulphonate in buffers. Conditions as in Table 1: ○, cacodylate buffers; △, acetate buffers; □, pyridine buffer

showed no initial deceleration for D_2O medium indicating no deuterium exchange.

A final deuterium exchange experiment involved analysis of the phenylmethanesulphonate product from deuterolysis of the 2,4-dinitrophenyl ester in pyridine buffer in deuterium

oxide. The ^1H content of the methylene group in the product (determined from peak area integrations of phenyl and methylene n.m.r. spectra) was found to be 1.2 and 1.3 for duplicate experiments as opposed to 2.0 in the control phenylmethanesulphonate ion. An error of *ca.* 0.1 is estimated in these results.

Mass Law Experiments with Added 2,4-Dinitrophenol.—The fission of 2,4-dinitrophenyl phenylmethanesulphonate (at *ca.* 10^{-5}M) was carried out in pyridine buffer at 2M concentration (fraction of base = 0.5; pH 5.3) in the presence and absence of 2,4-dinitrophenol. High absorbances coupled with a large expansion factor in the recording spectrophotometer gave considerable electronic 'noise' making it difficult to measure rate constants at reasonably high concentrations of the phenol. At a concentration of 2,4-dinitrophenol of 2.9×10^{-4}M there was a consistent decrease of the rate constant for ester fission below that without phenol additive; the accuracy of the results do not warrant a fuller study of the dependence of the rate at lower values of additive concentration. The rate constants are close to those expected for similar pyridine concentrations.[6] At low pyridine buffer concentration (0.1M) where formation of the carbanion is rate limiting (see later) no difference was observed between rate constants for the presence and absence of additive; the situation is even more difficult than at higher pyridine concentration because the rate constants are considerably lower and subject to more error.

TABLE 2

Hydrolysis of 2,4-dinitrophenyl-substituted phenylmethanesulphonates in media of varying composition

	Concentration of solute (M)	$10^3\ k/s^{-1}$
3-Nitrophenylmethane sulphonate		
Dioxan [a]	0	5.41
	1	4.08
	2	3.01
	4	2.47
Ethanol [a]	0.69	5.64, 5.56
	1.37	5.13, 5.10
	2.06	4.95
N-Methylpyridinium iodide [b]	0	5.42
	0.2	5.20
	0.4	4.94
	0.6	4.36
	1.0	4.15
KI [b]	0	5.42
	0.2	4.95
	0.4	4.37
	0.6	4.31
	0.8	3.88
	1.0	3.57
Pyrimidine [b]	0	5.42
	0.272	5.93
	0.532	5.63
	0.764	5.46
	0.996	4.96
Phenylmethanesulphonate		
Indole [c]	0	0.0585
	0.014	0.0543

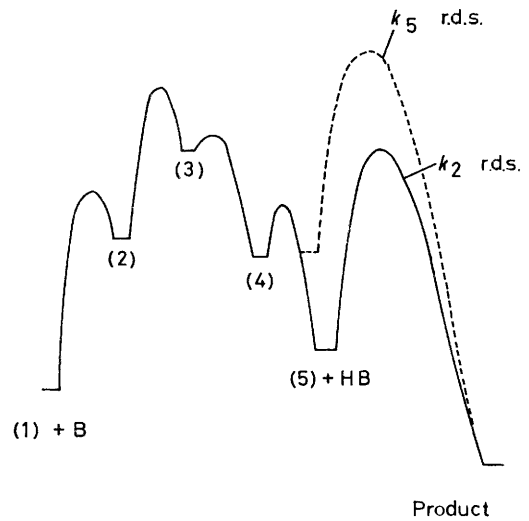
[a] Pyridine buffers at f.b. 0.5, 0.2M, 25 °C, pH 5.50, and ionic strength kept at 1M with KCl. [b] Solution kept at pH 7.13 with the pH-statted spectrophotometer cell, 25 °C, 4% v/v EtOH–water. [c] Pyridine buffer (0.04M), f.b. 0.5, pH 5.50, 7.6% v/v ethanol–water. The concentration of indole was measured spectrophotometrically at 296.5 nm using an extinction coefficient of 5 580 measured in a separate experiment. At 4% ethanol–water a species precipitated on adding substrate stock solution to the indole-containing buffer.

DISCUSSION

Buffer Curvature.—As the acidity of the leaving phenol increases a change in rate-limiting step occurs from breakdown of carbanion to its formation [1,2] in the hydrolysis of aryl phenylmethanesulphonates. Buffer curvature for 2,4-dinitrophenyl esters is not due to a change in rate limiting step from carbanion formation to decomposition because $k_{OH}^{max.}$ (6.18×10^5 l mol^{-1} s^{-1}) for 2,4-dinitrophenyl phenylmethanesulphonate is orders of magnitude lower than that expected for the $E1cB_r$ mechanism (2.7×10^9 l mol^{-1} s^{-1}). The latter parameter is calculated for aryl phenylmethanesulphonate hydrolysis in alkali from equation (3).[2c]

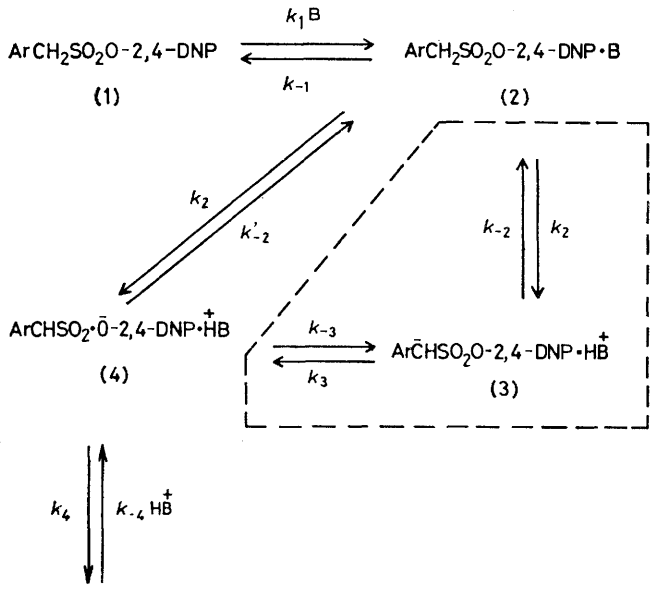
$$\log k_{OH}(E1cB_r) = 19.3 - 2.4\ pK_a^{ArOH} \qquad (3)$$

We propose that buffer curvature is due to a change in rate limiting step from the proton transfer (k_2) in the encounter complex (2) at low buffer concentration to decomposition of the sulphene–2,4-dinitrophenolate anion encounter complex (5) at high buffer concentration (Scheme 1). The full kinetic mechanism for Scheme 1 is given in equation (4). An alternative hypothesis is that k_4 is rate limiting at low buffer and k_5 at high buffer concentration; this would involve extensive S–O bond cleavage in the rate-limiting step not in agreement with the observed low selectivity of k_B to substituent in the leaving phenol;[2c] we conclude that $k'_{-2} < k_4$.



SCHEME 1 At low conjugate acid concentration k_2 is rate determining; at high conjugate acid concentration k_5 is rate limiting (dotted line)

We shall first consider the evidence that the buffer curvature is not due to specific solute or solvent effects. This problem is not insignificant because these effects occur at relatively high buffer concentration.[7] Added solutes tend to decrease the rate constant in a linear fashion (Figure 3). Control solutes which would not be involved in the reaction but which approximate to the



$$\text{ArCHSO}_2\cdot\bar{\text{O}}\text{-2,4-DNP} \xrightarrow{k_5} \text{Products} \qquad (4)$$
(5)

Compound in the ' cage ' is not a discrete species for esters with the 2,4-dinitrophenolate leaving group.

structure of pyridine and pyridinium ion are pyrimidine and *N*-methylpyridinium ion. It was most convenient to use the iodide salt of the latter species and the effect of added iodide ion was therefore measured; *N*-methylpyridinium ion tends to *increase* the rate constant after allowing for the effect of the iodide. We assume that the potassium ion has little effect on the reaction. Chloride ion concentration throughout the kinetics with pyridine buffer remains constant at 1M. The pyrimidine decreases the rate constant and coupled with the effect of *N*-methylpyridinium ion there is a net decrease of *ca.* 10% in the rate constant over a 1M range of concentration; this is compared with a 60% deviation from linearity in the hydrolysis of the 3-nitro-substituted ester.*

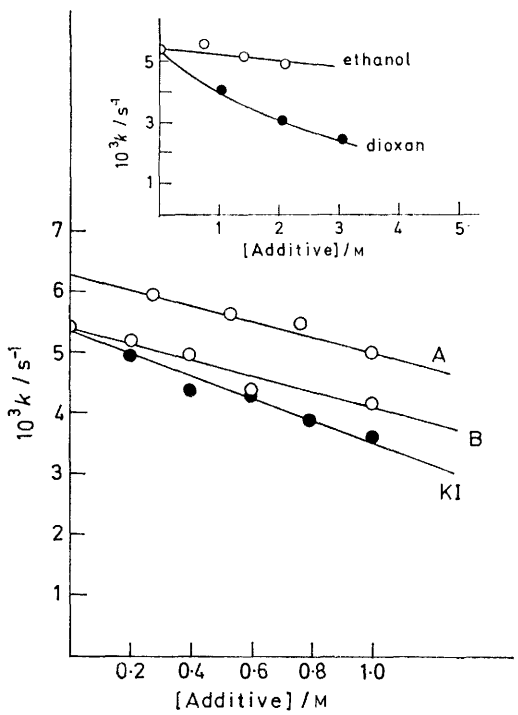


FIGURE 3 Effect of added solutes on the reaction of 2,4-dinitrophenyl 3-nitrophenylmethanesulphonate in aqueous buffer. A, Pyrimidine; B, *N*-methylpyridinium iodide. The data and conditions are in Table 2

The value of $k^{max.}$ is proportional to the hydroxide ion concentration (Figure 2) and is significantly independent of the buffer structure. Both of these observations are not consistent with the involvement of specific solute effects on the rate constants.

The absence of a significant effect on the hydrolysis of the sulphonate esters in the presence of indole a powerful ' charge transfer ' donor is evidence that complexation is probably not occurring between pyridine and the substrate other than in an encounter complex.

The following paper [6] reports measurements of the parameter K for pyridine against a series of 2,4-dinitrophenyl arylmethanesulphonate esters; there is a significant variation in K which is outside the experimental error involved in its determination. If the buffer curvature were due to a solute effect it should be the same for all substrates with a constant base–acid pair and lead to a constant value for K. We shall comment later on the cause of the variation in K. The value of K is indeed constant for a buffer when measured at different fractions of base (F.B.) as is required for the proposed mechanism but which is *not* consistent with a specific solute effect (see Table 2).

Vizgert *et al.*[8a] measured the hydroxide ion catalysed hydrolysis of phenyl arylmethanesulphonates [70% (v/v) dioxan–water; 40°] where the mechanism is known to be $E1cB_r$;[1a,2c] the Brønsted selectivity calculated from their work is −0.2 providing further evidence that the mechanism relating to high pyridine concentration is not $E1cB_r$ because $k_{OH}^{max.}$ has a Brønsted β value of −0.8.[6]

The kinetic scheme of equation (4) may be analysed assuming a steady-state concentration in the intermediates (2), (4), and (5) and this gives rise to a rate constant governed by equation (5). We know from previous studies [2] that the intermediate (3) has a lifetime less than that of an S–O bond vibration precluding its existence and forcing a concerted process from (2) to (4); we therefore treat these reactions [(2) ⟶ (4)] as a single one with forward and reverse rate constants k_2 and k'_{-2} [see equation (4)]. Equation (5) leads to curvature

$$k_{obs} = k_1k_2k_4k_5[B]/(k_{-1} + k_2)\{(k_4 + k'_{-2})k_5 + k'_{-2}k_{-4}[HB]\} \qquad (5)$$

in buffer plots and at large and small concentrations of [HB] it reduces to equations (6) and (7) respectively which correspond to the experimentally observed kinetic

* For details of the non-linear plot see Supplementary Publication No. SUP 22947 in ref. 6.

rate law [equation (2)]. Curvature in buffer plots is also seen with *NN*-dimethylaminoacetonitrile and *N*-propargylmorpholine [8b] but acids with pK_a values >7 show

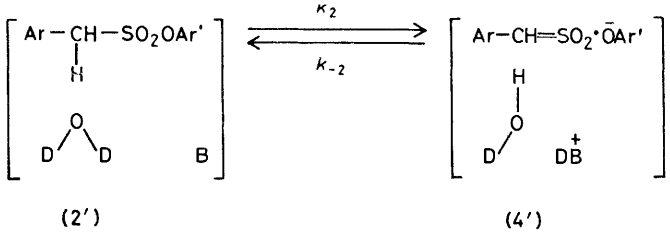
$$k_{obs} = k_1k_2k_4k_5[B]/(k_{-1} + k_2)k'_{-2}k_{-4}[HB] \quad (6)$$

$$k_{obs} = k_1k_2k_4[B]/(k_{-1} + k_2)(k_4 + k'_{-2}) \equiv k_B[B] \quad (7)$$

linear plots up to 1M concentration. The species of lower acidity will possess a lower value of k'_{-2} than those where curvature is observed; the return rate $[HB]k_{-4}$ must therefore be much larger in order to cause a change in rate-limiting step and for the acids in question the concentration required will be too high.

The absence of deuterium isotope exchange under conditions of large HB concentration is not consistent with the *E*1cB$_r$ mechanism. Entry of the deuterium isotope for exchange occurs by reaction of DB^+ with the intermediate (5) and a simple application of equation (5) indicates that at high general acid concentration deuterium should be incorporated in the methylene group of the reactant ester if the mechanism in Scheme 1 (including both pathways) is followed. Some form of internal return must operate in the series (1) ⟶ (2) ⟶ (4) so that despite exchange with solvent DB^+ the same ^1H atom is reincorporated in the ester reactant. Similar observations of the absence of deuterium isotope incorporation in high buffer concentrations have been reported for elimination reactions which are inhibited by the acidic component of the buffer catalyst. The DB^+ addition step (k_{-4}) leads through (4) and (2) to (1) faster than the forward reaction to product at high concentration of DB^+. The 'reprotonation' cannot be slower than the forward rate constant (k_5), otherwise the latter would not be rate limiting. We propose a scheme, similar to that of Crowell and his co-workers,[5a] where a water or deuterium oxide bridge relays a proton to the base from the methylene group and allows the DB^+ to equilibrate with the medium DB^+ while retaining the ^1H which has been transferred.

It is necessary that the DOH species in (4') equilibrates only slowly with solvent D_2O and that rotational isomerisation to expose the ^1H in (4') of Scheme 2 is slow relative



(2') (4')

SCHEME 2

to the forward reaction (k_4) which is a diffusion step. There is precedence for a rotational isomerisation reaction which is slower than diffusion occurring in an encounter complex. Ivin and his co-workers [9] observed a relaxation time corresponding to a rate constant ($<4 \times 10^9$ s^{-1}) limiting the rate of proton transfer from 2,4-dinitrophenol to a tertiary amine; the rate constant was ascribed to a reorganisational isomerisation in the encounter complex. The rotational rate constants of individual polar molecules are in the region of 10^{11} s^{-1} for the gas phase.[9]

The assumption that water (HOD) does not exchange with solvent more rapidly than the forward reaction has several precedents in analogous systems. Grunwald and Ralph [10] indicate that solvation complexes of hydroxylic solvents with amine exchange with solvent at a rate slower than diffusion. There is also considerable experience of internal return mechanisms where exchange of a carbon acid with a deuteriated solvent may be slower than ionisation;[11] the occurrence of carbanion ion pairs and tightly solvated carbanions is well established in proton transfer reactions to carbon.[11]

The participation of solvent molecules as relay agents for proton transfer reactions has been considered for some time [12] and direct evidence was first obtained by Grunwald *et al.* for proton exchange between amine molecules *via* water.[13] Solvent participation is very common with proton transfer between oxygen or nitrogen bases.[12] Cyanocarbon and sulphone-carbon acids show proton-transfer behaviour which is virtually the same as for oxygen or nitrogen acids of comparable strength;[14,15] these carbon acids differ from nitroparaffins, β-diketones, and azulinium ions where proton transfer is notably slow and it is supposed [14] that this may be due to the dispersion of the negative charge far from the reactive site.

The relay proton transfer mechanism requires that there is less interaction between sulphene and the acid HB^+ in the complex (4) than between sulphene and the water relay. The presence of a significant excess of ^1H over 50% incorporation in the product would agree with a relatively strong sulphene–water complex.

A final requirement of the mechanism is that the 2,4-dinitrophenolate anion diffuses from the complex more slowly than the acid. This requirement is reasonable since the phenolate oxyanion is generated close to the highly electrophilic $=SO_2$ centre; such analogues as exist (sulphur trioxide and sulphenimines) are known to be powerful electrophiles.[16,17]

The mechanism which we propose is closely similar to that of Crowell and his co-workers [5a] which has been criticised in a recent review.[18] It is very difficult to ascribe the results of this and the accompanying work [6] in terms of anything related to specific solute effects and the criticism of the similar Crowell mechanism [18] was directed at the lifetime of an ethoxonium–carbanion ion pair in ethanol. We should point out that we are only proposing that the lifetime of our 'stable' species are *relative* to *diffusion processes* and are therefore more acceptable in the light of these criticisms because the latter processes are very fast.

It should be noted that the deuterium isotope exchange observed by King and Beatson [1a] in the hydrolysis of 2-chloro-4-nitrophenyl phenylmethanesulphonate is probably due to the rate-limiting step being carbanion decomposition; 2-chloro-4-nitrophenol has a pK_a close

to that for the changeover from irreversible to reversible *E*1cB mechanisms.

Individual Rate Constants for the Kinetic Scheme.—The kinetic scheme of equation (4) modified to allow for the concerted step from (2) to (4) possesses a number of rate constants which may be identified at least to within an order of magnitude; k_1, k_{-1}, k_4, and k_{-4} are essentially diffusion processes and the only unknowns are k_2, k'_{-2}, and k_5. Equation (7) indicates that k_{pyr} is a complex function but the relationship that $k'_{-2} < k_4$ (see earlier) simplifies the function to equation (8). Equation (6) for high buffer concentration reduces to equation (9).

$$k_{pyr} = k_1k_2/(k_{-1} + k_2) \quad (8)$$

$$k_{obs} = k_1k_2k_4k_5K_a[OH]/(k_{-1} + k_2)k'_{-2}k_{-4}K_w = k_{OH}^{max.}[OH^-] \quad (9)$$

The value of K [see equation (2)] is essentially equal to the value of the concentration of HB^+ at $k_{obs} = \frac{1}{2}k^{max.}$. Perusal of equation (5) indicates that this parameter is related according to equation (10). Both k_5 and

$$K = k_5(k_4 + k'_{-2})/k'_{-2}k_{-4} = k_4k_5/k_{-4}k'_{-2} \quad (10)$$

k'_{-2} relate to a reaction of a nucleophile with the sulphene and k_4/k_{-4} is substituent invariant; the value of K might therefore be expected to be only slightly dependent on the substituent in the phenylmethane group and this is illustrated in Figure 4.

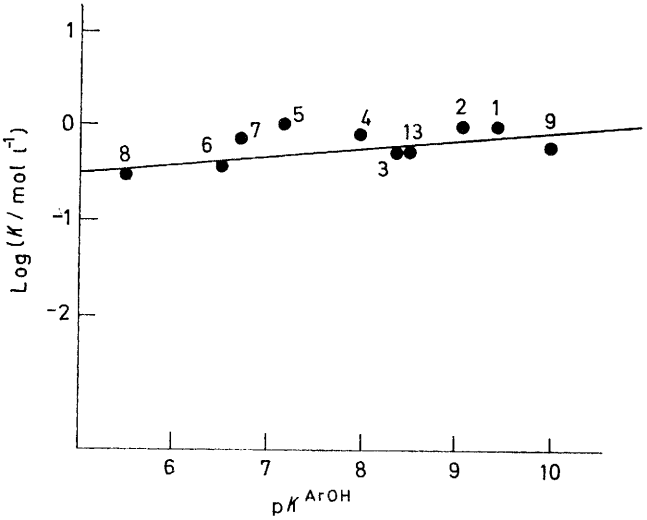


FIGURE 4 Dependence of log K on the pK of the phenol corresponding to the phenyl substituent for the reaction of 2,4-dinitrophenyl-substituted phenylmethanesulphonate in pyridine buffers. Data are taken from the following paper [6]

We are now in a position to discuss the possibility suggested by King and Beatson [13] that exchange at the α-carbon could occur *via* reversal from the sulphene. Deuterium exchange certainly occurs with phenylmethanesulphonate esters of phenols with pK >7;* for these esters the concerted pathway does not occur and the carbanion (3) exists as a true intermediate. If (3) survives for long enough for diffusion to exchange HB for DB and ' relay ' solvent then exchange will occur *via* the carbanion; however, there is a range of more acidic leaving phenols where the formation of sulphene (4) is more efficient than the diffusion process and for these esters exchange will be *via* the sulphene as it is for the ' *E*2 ' substrates but of course internal return will occur if the decomposition of the sulphene encounter complex is faster than the exchange of the ' relay ' solvent.

The rate constant for decomposition of the sulphene complex with 2,4-dinitrophenolate anion must be a non-diffusion controlled process, otherwise no change in rate-limiting step will occur on increasing HB concentration. Clearly the exchange of 2,4-dinitrophenolate anion for water is a diffusion process but the reaction step is relatively slow. It is unlikely that pyridine will be important as a nucleophile because the products of this reaction with the sulphene, *i.e.* the *N*-sulphonylpyridine will revert rapidly to sulphene and will not provide an alternative pathway for decomposition. We suggest that the sulphene although not decomposing as fast as a diffusion-controlled process is nonetheless very reactive.

S_NAr Attack by the buffer components as a cause of buffer curvature is ruled out by isotope incorporation experiments and other arguments.[8b] The mass law experiments where added 2,4-dinitrophenol decreases the rate constant for hydrolysis of 2,4-dinitrophenyl phenylmethanesulphonate at high pyridine concentration is also consistent with the absence of an S_NAr mechanism and fits Scheme 1; at low pyridine concentration where formation of (4) is rate limiting no effect of added 2,4-dinitrophenol is observed on the rate constant in accord with Scheme 1. The latter conclusions must be tempered with the knowledge that the error is close to being unacceptable (see Results section).

So far as we are aware there are very few well authenticated cases of extensive internal return during acid inhibition of elimination. This work and that of Crowell and his co-workers [5a] merits further study and we are at present engaged on a stereochemical investigation of the problem.

We are grateful to the British Council and the S.R.C. for financial support.

[0/875 *Received*, 9*th June*, 1980]

* Exchange in deuterium oxide was used to synthesise esters fully deuteriated at the methylene group for studies on the primary isotope effect.[2c]

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