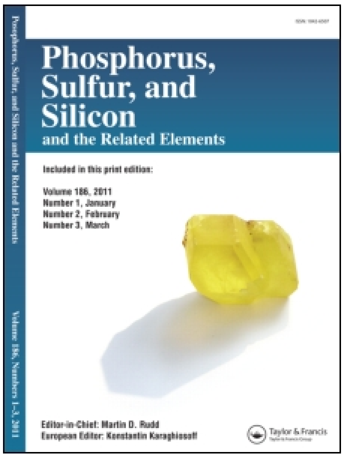

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A PROTON INVENTORY STUDY OF THE WATER-CATALYSED HYDROLYSIS OF A SULPHITE ESTER IN AQUEOUS DIOXANE

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The water-catalysed (spontaneous) hydrolysis of bis(*p*-nitrophenyl) sulphite in aqueous dioxane exhibits a solvent deuterium isotope effect of $k_{H_2O}/k_{D_2O} = 3.21$ and is second order in water concentration. The proton inventory plot for mixtures of protium oxide—deuterium oxide shows significant downward curvature and suggests the involvement of three equivalent protons. Several possible transition states are considered.

Key words: Proton inventory; sulphite ester hydrolysis.

INTRODUCTION

The water-catalysed (spontaneous) hydrolyses of a number of carboxylic acid derivatives have been studied in some detail as models for biological systems in which acyl transfer and hydrolysis reactions are of considerable importance.[1] Increasing interest has recently been shown in the corresponding nucleophilic reactions of sulphite esters. Several groups have investigated the pepsin-catalysed hydrolysis of sulphites[2–4] and a kinetic study of metal ion catalysis has also been reported.[5]

Whilst nucleophilic reactions of carboxylic ester derivatives are generally thought to proceed via formation of a tetrahedral intermediate,[6] nucleophilic substitution at sulphinyl sulphur may occur via a concerted or a stepwise mechanism.[7] Although O^{18}-exchange experiments failed to establish the formation of a covalent intermediate in the alkaline hydrolysis of sulphite esters[8] (but did not exclude their formation), Kaiser and his co-workers have demonstrated, by both spectroscopic and trapping techniques, the formation of a mixed carboxylic-sulphurous anhydride intermediate in the reaction of diaryl sulphites with carboxylic acid buffers.[3,9] To provide a more detailed picture of nucleophilic displacement at sulphinyl sulphur we now report a proton inventory study of the spontaneous hydrolysis of bis(*p*-nitrophenyl) sulphite, **1**, in aqueous dioxane.

EXPERIMENTAL

Materials. Bis(*p*-nitrophenyl) sulphite was prepared from 4-nitrophenol and thionyl chloride by the literature method[10] and had m.p. 104–105° (lit[10]., 98–100°). Deuterium oxide (99.8 atom %

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deuterium, Aldrich Gold Label) was used as obtained. Solutions for the water order and proton inventory kinetic experiments were made up by weight (in the latter case to produce a constant mole fraction of dioxane equal to 0.24).

Kinetic Measurements. The hydrolysis of **1** was monitored by following the appearance of 4-nitrophenol at 320 nm on a Perkin Elmer model 554 u.v. spectrometer equipped with a thermostatted cell block (±0.05°C). In view of the need for optimum temperature control the cell compartment itself was additionally thermostatted. Reactions were initiated by the addition of 10 μl of stock solution in dioxane (freshly prepared daily) to 3.00 mL of the appropriate reaction solution to give a substrate concentration of ca. 4×10^{-5} *M*. Reactions were followed for more than three half-lives. Values of the first-order rate coefficients were calculated using a non-linear least squares computer program and are shown in Figure 1 and Tables I–III.

DISCUSSION

Values of the first-order rate coefficients, k_1, for the hydrolysis of (**1**) in weakly acidic dioxane containing either protium oxide or deuterium oxide are shown in Table I. As for the hydrolysis of diphenyl sulphite, the pH-rate profile for the hydrolysis of **1** in both solvents shows a distinct plateau region which can be attributed to water-catalysed (spontaneous) hydrolysis. The value of the solvent deuterium isotope effect, k_{H_2O}/k_{D_2O}, for this pH-independent reaction is 3.21. Similar values of k_{H_2O}/k_{D_2O} have been observed for the spontaneous hydrolysis of

TABLE I

First-order rate coefficients for the hydrolysis of **1** in dioxane containing dilute solutions of H_2O or D_2O at 30.0 ± 0.05°C[a]

$[H^+]/M$	$[LiClO_4]M$	$10^5k^b_{H_2O}/m^{-1}$	$10^5k^b_{D_2O}/m^{-1}$
0.100	—	8473 ± 140	2509 ± 26
0.040	0.060	8314 ± 57	2539 ± 22
0.010	0.090	7986 ± 96	2445 ± 24
0.004	0.096	8124 ± 39	2533 ± 14
0.002	0.098	8314 ± 25	2523 ± 21
0.001	0.099	8201 ± 79	2592 ± 12

[a] The mole fraction for dioxane was 0.240; ionic strength 0.100.
[b] Error limits are standard deviations.

TABLE II

First-order rate coefficients for the hydrolysis of **1** in aqueous dioxane as a function of water concentration at 30.0 ± 0.05°C[a]

$[H_2O]M$	$10^5k^b_1/m^{-1}$
19.00	5363 ± 79
20.00	6159 ± 75
21.00	7096 ± 143
22.00	7499 ± 95
23.00	8344 ± 97
24.00	9081 ± 45
25.00	10045 ± 148

[a] Ionic strength maintained at 0.100 with addition of $LiClO_4$.
[b] Error limits are standard deviations.

TABLE III

First-order rate coefficients for the "water" hydrolysis of **1** at 30.0 ± 0.05°C and $\mu = 0.100$ in H_2O–D_2O mixtures of atom fraction deuterium (n)[a]

n	$10^5k_1^b/\text{m}^{-1}$	n	$10^5k_1^b/\text{m}^{-1}$
0.000	8377 ± 69	0.496	4879 ± 11
0.101	7406 ± 97	0.596	4248 ± 66
0.200	6983 ± 69	0.703	3877 ± 26
0.253	6404 ± 53	0.796	3369 ± 16
0.297	6171 ± 47	0.998	2610 ± 26

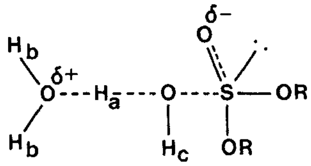
[a] With added $HClO_4$ (0.05M) and $LiClO_4$ (0.05M).

[b] Average of three determinations, error limits shown are standard deviations.

a variety of carboxylic acid derivatives e.g. acetic anhydride, 2.90[11] and p-nitrophenyl dichloroacetate, 3.10.[12] A somewhat lower value (2.20) was observed for the hydrolysis of bis(p-nitrophenyl) carbonate.[13]

The hydrolysis of **1** has also been studied in aqueous dioxane mixtures of varying water concentration whilst the ionic strength was maintained constant. The water order plot of $\log k_1$, *versus* $\log [H_2O]$ produces a straight line of slope 2.2 (±0.1) with a correlation coefficient (r) of 0.996. This result suggests a second-order dependence on water for the hydrolysis of **1** and is similar to that (2.13) observed for the corresponding carbonate ester.[13]

It is convenient to consider here one model of the transition state for the hydrolysis of **1** which would be consistent with a second-order dependence—the classic 'proton-bridge' transition state structure **2** analogous to that proposed for the hydrolysis of various acyl derivatives[12] in which one water molecule serves as a general base and the other as a nucleophile which in this case attacks the central sulphur atom via a triginal bipyramidal geometry.



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The proton inventory technique has been well documented[14,15] and involves the measurement of rate coefficients (k_n) in mixtures of protium oxide and deuterium oxide of various deuterium atom fractions. The observed rate constant, k_n, is related to the rate constant, k_0, in pure protium oxide by the Gross–Butler equation (Equation (1)) where the contributions of i exchangeable transition

$$k_n = k_0 \prod_{i}^{\text{T.S.}} (1 - n + n\phi_i^*) \Big/ \prod_{j}^{\text{R.S.}} (1 - n + n\phi_j) \qquad (1)$$

state (T.S.) protons) and j exchangeable reactant state (R.S.) protons are characterised by their respective fractionation factors ϕ_i^* and ϕ_j and contribute as

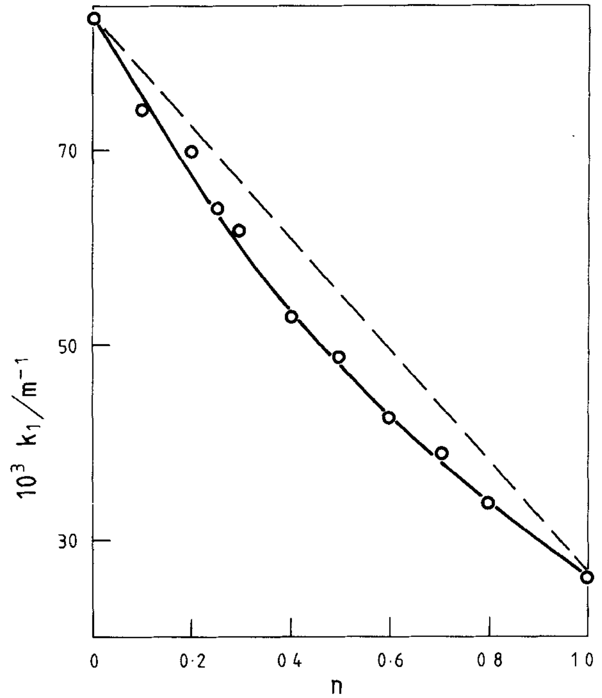


FIGURE 1 Dependence of the observed first-order rate coefficient for the hydrolysis of **1** on the atom fraction of deuterium in the solvent (data from Table III). The dashed line is included to emphasize the nonlinear nature of the data.

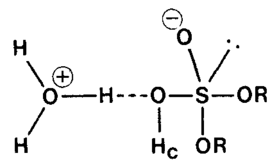
shown to the observed solvent isotope effect. In the present case all the exchangeable reactant state sites are solvent sites for which by definition $\phi_j = 1$, hence Equation (1) reduces to Equation (2).

$$k_n = k_0 \prod_i^{\text{T.S.}} (1 - n + n\phi_i^*) \tag{2}$$

The significant curvature for the proton inventory plot (Figure 1) for the hydrolysis of **1** suggests that more than one proton contributes to the solvent deuterium isotope effect on the rate-determining transition state. The observed curvature can be analysed by Schowen's method[14] or by Albery's 'γ' treatment. Using Schowen's approach, the goodness of fit of various mathematical models were examined in terms of (a) residual sum of squares, (b) standard deviation, (c) F-statistic (or partial-F) and (d) residual analysis tests. On the basis of all these criteria the best fit was achieved by a cubic equation (Equation (3)) with $\phi^* = 0.68$

$$k_n = k_0(1 - n + \phi^* n)^3 \tag{3}$$

Such a relationship would not be expected for the 'proton-bridge' transition state proposed in **2**. In principle, the model **2** has four isotopically exchangeable protons which could contribute to the observed isotope effect. The 'in-flight' proton (H_a) being transferred to the water molecule acting as a general base should contribute a primary solvent isotope effect to the overall effect and would



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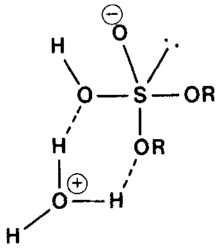

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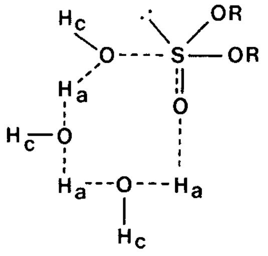

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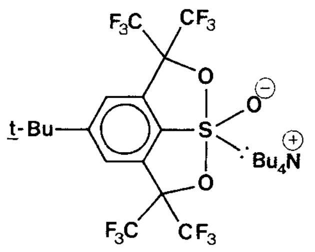

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typically be expected to have a value of around 0.5. The proton H_c is assumed to have a value of unity. The two H_b protons will contribute secondary isotope effects and may be expected to have values which lie between unity (if no transfer of H_a occurs) and 0.69 (if H_a is fully transferred to produce a fully developed hydronium ion). For the transition state **2**, therefore, a relationship of the form shown in Equation (4) would be expected.

$$k_n = k_0(1 - n + n\phi_a^*)(1 - n + n\phi_b^*)^2 \tag{4}$$

The observed 'best-fit' cubic Equation (3) which generates the experimental proton inventory curve suggests a transition state with three equivalent protons with fractionation factors of 0.69 which is the value for the hydronium ion. Two such possible transition states are **3** which is a 'very late' form of **2**, the transition state for formation of a pentacovalent intermediate and **4**, a 'very early' transition state for break down of this intermediate. Similar alternatives have been discussed for the hydrolysis of phthalic anhydride.[16]

Strictly, a term of the form $(1 - n + \phi_c^* n)$ should be included in Equation (3) for the H_c proton. Analogous gem-diol protons arising from a similar situation in acyl derivatives typically show fractionation factors in the range 1.21 to 1.28.[17] In the absence of any evidence we have assumed $\phi_c \sim 1.00$. The precision of our rate constants is, in any case, less than that required (ca. 0.7%) to distinguish between a three-proton and a four-proton fit.

Another possible transition state which would be consistent with a cubic equation and in which three protons contribute equally to the solvent isotope effect is shown in **5**. This involves eight atoms in a cyclic array considered to be a favoured requirement for proton transfer by Gandour.[18] This structure is not, however, consistent with the observed second-order dependence on water concentration or the magnitude of the fractionation factors obtained.

Additional information about the structures of transition states of water reactions can often be obtained from Brönsted plots. To date, no sysematic study of the reactions of nucleophiles with bis(p-nitrophenyl) sulphite, **1**, has been reported. It has been shown however, that for the reaction of a variety of nucleophiles with diphenyl sulphite the water point does lie approximately on the Brönsted plot giving a β value of 0.71.[4] It is tempting to assume that this value, which indicates a later transition state than that observed for the corresponding carbonates[19] ($\beta = 0.36$), is general for the reaction of all sulphite esters and is consistent with the late transition state **3** proposed for the hydrolysis of **1**. It is interesting to note the close similarity in the structure of **3** and that of the bicyclic 10-S-4 sulphuranoxide sulphurane **6** isolated by Martin and his co-workers from alkaline hydrolysis of the precursor cyclic sulphinate.[20]

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