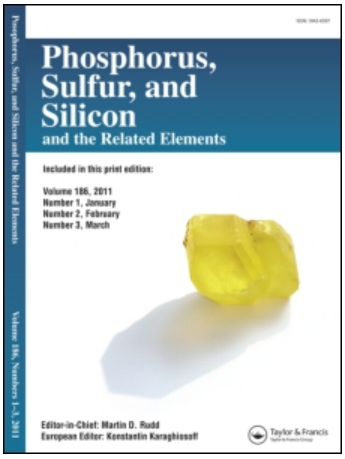

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ACID-CATALYSED HYDROLYSIS AND ALCOHOLYSIS OF 4-NITROPHENYL-*N*-ACETYL-PHENYLIMINOSULPHONATE

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ACID-CATALYSED HYDROLYSIS AND ALCOHOLYSIS OF 4-NITROPHENYL-*N*-ACETYL-PHENYLIMINOSULPHONATE

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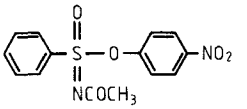
The acid-catalysed hydrolysis of the title compound (**1**) has been studied in aqueous (20% v/v) dioxane solutions of mineral acids. The kinetic data were analysed in terms of the Bunnett-Olsen approach, activation parameters and solvent isotope effects and were consistent with a bimolecular (A-2) mechanism. The kinetics and products of alcoholysis of **1** have also been investigated.

INTRODUCTION

A study of the kinetics and mechanism of the alkaline hydrolysis of *N*-acyl-areneiminosulphonate esters has recently been reported from this laboratory.[1] Hydrolysis in alkali proceeds via nucleophilic substitution at sulphur. Levchenko and her co-workers have reported that such esters are stable to prolonged boiling in water or dilute acid.[2] We now report the first kinetic study of the acid-catalysed hydrolysis of this class of compound on 4-nitrophenyl-*N*-acetylphenyliminsulphonate, (**1**), which is much less resistant to acid hydrolysis than its *N*-benzoyl analogue.



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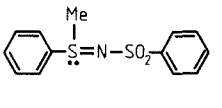

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RESULTS AND DISCUSSION

The first-order rate constants, k_1, for the hydrolysis of **1** in aqueous (20% v/v) dioxane solutions of mineral acids are shown in Figure 1. At low acidity the rates of hydrolysis are similar in all four acids studied and do not depend on the nucleophilicity of the acid anion suggesting that nucleophilic catalysis (particularly by halide ions) which is so prevalent in the acid-catalysed reaction of sulphinyl (>S=O) compounds[3] is relatively unimportant in the sulphinimidoyl system. At

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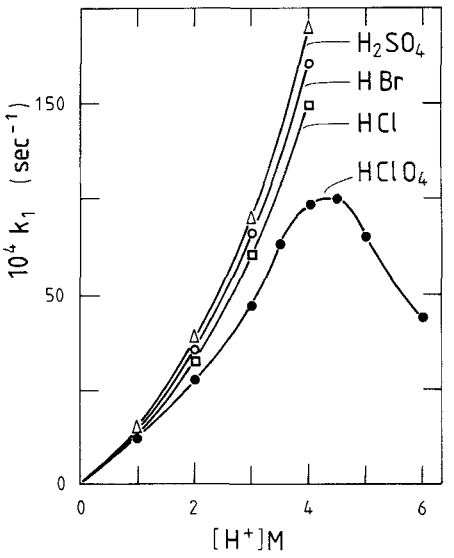


FIGURE 1 Plots of k_1 for acid-catalysed hydrolysis of **1** in aqueous (20% v/v) dioxane at 25.0°: $HClO_4$ ●; H_2SO_4 Δ; HBr ○; HCl □.

higher concentrations of perchloric acid (>4.0 Molar) the rate of hydrolysis of **1** goes through a maximum. Similar behaviour has been observed for the acid-catalysed hydrolysis of amides[4] and *N*-sulphonyl sulphilimines (**2**)[5] and has been attributed to extensive protonation of the substrate accompanying the decreasing value of a_{H_2O} with increasing acid concentration.

A more detailed study of the kinetic behaviour at low acidity (Table I) shows that the rates of hydrolysis increase more rapidly than does acid concentration presumably due to a positive salt effect. Such behaviour is characteristic of many reactions proceeding by an A-2 mechanism e.g. the acid-catalysed hydrolyses of ethyl acetate[6] and episulphoxides.[7]

Analysis of the kinetic data at low acidity in terms of the Bunnett w and w^* treatments[8] gives plots of considerable scatter. However, use of the Bunnett-Olsen linear free energy approach[9] gives good straight line plots of $\log k_1 + H_0$ versus $(H_0 + \log [H^+])$ with slopes ϕ of 0.95 (corr. coefft. r, 0.997) and 0.72 (r, 0.999) for perchloric and sulphuric acids respectively. Such values of ϕ

TABLE I

Rate constants for hydrolysis of **1** in aqueous (20% v/v) dioxane at 25.0°

$[HClO_4]$/M	0.560	0.830	1.12	1.40	1.68
$10^4 k_1$ (sec^{-1})	9.07	15.0	18.2	25.0	27.5
$[HClO_4]$/M	1.96	2.24	2.52	2.80	3.36
$10^4 k_1$ (sec^{-1})	34.4	37.1	45.7	50.2	61.3
$[H_2SO_4]$/M	0.432	0.865	1.30	1.73	2.16
$10^4 k_1$ (sec^{-1})	6.69	13.6	22.0	32.7	44.8
$[H_2SO_4]$/M	2.59	3.02	3.46	3.89	4.32
$10^4 k_1$ (sec^{-1})	56.4	75.3	91.8	115	147

TABLE II

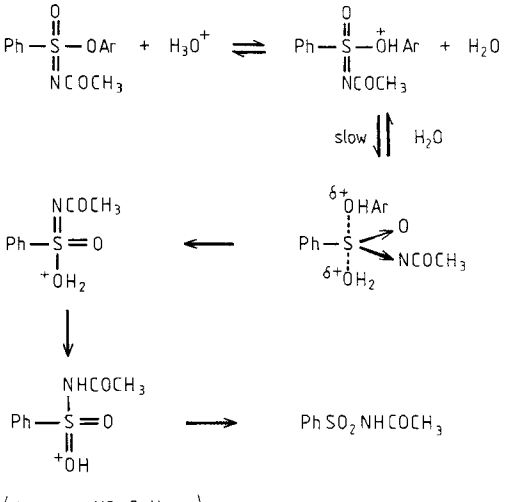
Rate constants and Arrhenius parameters for hydrolysis of **1** in aqueous (20% v/v) dioxane at different temperatures

T°C	25.0	29.6	34.6	39.4	44.7	50.0
$HClO_4$, $10^4 k_1$ (sec^{-1})	13.0	19.1	29.3	43.2	65.2	96.9
T°C	20.0	25.0	30.6	35.0	40.0	—
HCl, $10^4 k_1$ (sec^{-1})	8.40	14.0	22.1	31.4	51.1	—

	$HClO_4$ (0.89 M)	HCl (1.00 M)
$\Delta H^{\ddagger}$ (kcal. mol^{-1})	14.8 ± 0.1	15.5 ± 0.4
$\Delta S^{\ddagger}$ (cal. deg. mol^{-1})	-22.0 ± 0.2	-19.7 ± 1.4

correspond to a high degree of participation of water molecules in the transition state and fall in the range typically associated with a mechanism in which water behaves both as a nucleophile and a proton transfer agent. However, O'Connor has suggested[10] that the limits of ϕ for the A-2 mechanism of hydrolysis of amides should be extended to $0.47 \leqq \phi \leqq 0.98$. In a similar way values of ϕ in the range 0.63–0.81 for the acid-catalysed hydrolysis of diarylisosydnones have also been attributed to an A-2 mechanism. The values of the entropy of activation ($\Delta S^{\ddagger} = -22$ and -19.7 cal. $deg^{-1}\,mol^{-1}$ for perchloric and hydrochloric acids respectively) (Table II) are also consistent with a bimolecular rate-determining step.[12]

The values of the kinetic solvent isotope effect ($k_1^{D_2O}/k_1^{H_2O} = 1.77$, 1.62 and 1.39 for 1.00 M hydrochloric, perchloric and sulphuric acids respectively) are typical of reactions which proceed via a rapid pre-equilibrium proton transfer.[13] At the present time there is no direct evidence for the site of protonation of **1** which could be nitrogen or oxygen. An A-2 mechanism which assumes protonation on oxygen and a rate-determining steps involving attack of water at sulphur is shown in Scheme 1.



Scheme 1

It is of interest to compare the reactivity of **1** towards acid hydrolysis with that of other analogous sulphonyl systems such as *p*-nitrophenyl benzenesulphonate. Hydrolysis of this sulphonate, however, requires rather extreme conditions such as heating with 10 N hydrochloric acid in a sealed tube above 160°C[14]. The enormous difference in reactivity on going from the —SO_2— group in the O=S=NCOR system must result from a combination of the much greater activation of the central sulphur atom by the =NCOR group and the exceptionally low basicity of sulphonate esters.

ALCOHOLYSIS

We have also studied the kinetics of the acid-catalysed reaction of **1** with alcohols using the alcohol as solvent. The required amount of hydrogen chloride gas was bubbled through the alcohol and its concentration checked by titration for each run. Good first-order plots were obtained, the reaction rates were linearly dependent on the concentration of hydrogen chloride added and dependent on the alcohol used (Figure 2).

The reactivity of alcohols depends on a number of different factors. In the present case, steric effects which will be greatest for iso-propanol seem to play a dominant role. This is confirmed by the much less favourable value of the entropy of activation for this reactant (Table III). Analysis of the product mixture shows the products to be 4-nitrophenol and *N*-acetylbenzenesulphonamide. These observations suggest initial formation of the methyl ester which is not isolated but decomposes rapidly under the reaction conditions (Equation 1). The solvolyses of

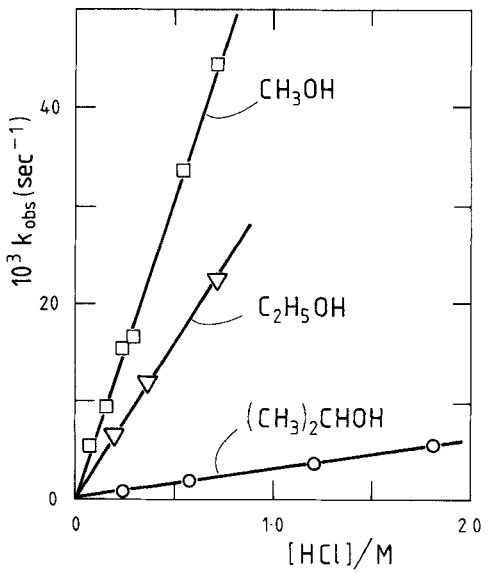


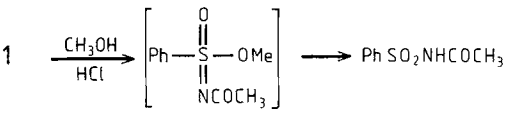
FIGURE 2 Plots of k_1 *versus* hydrochloric acid concentration for the reaction of alcohols with **1** at 25.0°: methanol □, ethanol ▽, isopropanol ○.

TABLE III

Rate constants and Arrhenius parameters for the hydrochloric acid-catalysed reaction of **1** with alcohols at different temperatures

(a) MeOH (0.250 M HCl)					
T°C	19.8	23.0	25.0	31.0	36.0
$10^3 k_1$ (sec^{-1})	9.55	12.7	15.5	24.0	38.0
(b) EtOH (0.200 M HCl)					
T°C	21.2	25.0	29.8	34.4	43.6
$10^3 k_1$ (sec^{-1})	4.52	6.55	9.18	13.8	25.3
(c) *i*-PrOH (1.20 M HCl)					
T°C	25.0	31.0	36.0	43.1	
$10^3 k_1$ (sec^{-1})	36.8	5.09	6.82	10.0	

Alcohol	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal deg^{-1} mol^{-1})
MeOH	14.5 ± 0.4	−18.3 ± 1.3
EtOH	13.9 ± 0.4	−23.0 ± 1.3
i-PrOH	10.2 ± 0.3	−35.5 ± 1.1



(1)

N-alkylsulphonimidoyl chlorides in methanol also lead to formation of the corresponding sulphonamides and are considered to involve a similar ester intermediate.[15]

Levchenko and her co-workers have pointed out that the reactivity of arenesulphonimidic esters and acid chlorides towards acid hydrolysis and hydrogen chloride depends critically on the nature of the substituent on the imino group.[1] *N*-alkyl derivatives react quite readily whilst *N*-benzoyl derivatives are relatively unreactive. *N*-acetylarenesulphonimidic esters show reactivity which more closely resembles that of the corresponding *N*-alkyl sulphonimidates.

EXPERIMENTAL

Materials Solvents and acids used were of Analar quality. The synthesis and properties of **1** have been reported previously.[1]

Kinetic procedure The rates of hydrolysis and alcoholysis were determined spectrophotometrically at 315 nm using a Perkin-Elmer model 554 u.v. spectrometer with a thermostatted cell compartment (±0.05°C). Substrate (50 μL in dioxane) was added to 3.0 ml of the appropriate medium in a 1 cm pathlength quartz cell at the required temperature. The concentration of **1** used was *ca.* 1×10^{-4} M. Good first-order behaviour was observed with a clean isosbestic point. Values of k_1 were calculated from the standard equation using a least-squares procedure.

Product Analysis The u.v. spectra of the products of hydrolysis and alcoholysis ([**1**] = 4.32×10^{-3} M) in 0.20 M HCl were shown to be identical to that of an equimolar mixture of 4-nitrophenol and *N*-acetylbenzenesulphonamide.

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