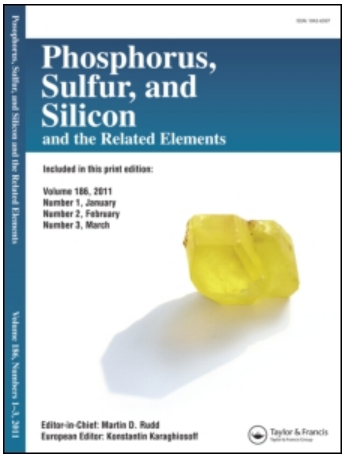


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# KINETICS AND MECHANISMS OF THE ACID- CATALYSED HYDROLYSES OF 4-NITROPHENYL- N-AROYL-ARENEIMINOSULPHONATES

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# KINETICS AND MECHANISMS OF THE ACID-CATALYSED HYDROLYSES OF 4-NITROPHENYL-N-AROYL-ARENEIMINOSULPHONATES

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The acid catalysed hydrolyses of N-acetyl and a series of N-aroylsulphonimidic esters have been studied in aqueous 40% (v/v) dioxane solutions of mineral acids. At low acidity all the esters studied are considered to hydrolyse by an A-2 mechanism. At higher acidities a changeover to an A-1 mechanism is observed for N-aroylsulphonimidic esters.

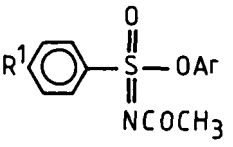
*Key words:* Acid-catalysed hydrolysis; sulphonimidic esters.

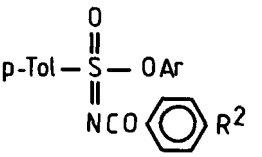


## INTRODUCTION

A study of the kinetics and mechanism of hydrolysis of 4-nitrophenyl-N-acetyl-phenyliminosulphonate (**1a**) in aqueous (20% v/v) dioxane solutions of mineral acids has previously been reported from this laboratory.[1]

The hydrolysis of **1a** exhibited a rate maximum in perchloric acid (~4.0 M) and the order of effectiveness of added acids ([$H^+$] = 2.00 M) was $H_2SO_4$ > HCl > $HClO_4$. These data and values of the entropy of activation ($\Delta S\ddagger$) for hydrolysis in





**1** a ; $R^1$ = H

b ; $R^1$ = Me

(Ar = p-$NO_2C_6H_4$—)

**2** a ; $R^2$ = MeO

b ; $R^2$ = Me

c ; $R^2$ = H

d ; $R^2$ = Cl

e ; $R^2$ = $NO_2$

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both perchloric and hydrochloric acids at low acidity (<1.0 M) ( −22.0 and −19.7 cal.deg$^{-1}$mol$^{-1}$) were consistent with a bimolecular (A-2) mechanism involving attack by water at the central sulphur atom of the protonated sulphonimidic ester. We now report a complementary study of the acid-catalysed hydrolysis in aqueous (40% v/v) dioxane of a series of N-aroyl-*p*-toluenesulphonimidic esters (**2a–e**; $R^2$ = MeO, Me, H, Cl, $NO_2$), the members of which are more resistant to acid hydrolysis than their N-acetyl analogue whose hydrolysis in this solvent has also been studied.

## RESULTS AND DISCUSSION

The first-order rate coefficients, $k_1$, for the hydrolysis of p-nitrophenyl N-acetyl-*p*-tolueneiminosulphonate (**1b**) in aqueous 40% (v/v) dioxane solutions of mineral acids are shown in Figure 1. The kinetic behaviour is very similar to that reported for the hydrolysis of the corresponding phenyl system (**1a**) in 20% aqueous (v/v) dioxane.[1] Rate maxima are observed for both perchloric and sulphuric acid since hydrolysis was studied over a wider range of acidity. Similar behaviour has been observed for the hydrolyses of amides[2] and N-sulphonyl sulphilimines[3] and has been attributed to extensive protonation of a substrate accompanied by the decreasing value of $a_{H_2O}$ with increasing acid concentration. Values of the entropy of activation for the hydrolysis of **1b** ($\Delta S\ddagger$ = −13.1, −15.1 and −14.7 cal.deg$^{-1}$mol$^{-1}$ for perchloric, hydrochloric and sulphuric acids respectively Table III) are also consistent with a bimolecular mechanism. These data confirm that the mechanisms of hydrolysis of N-acetylsulphonimidic esters are similar in both 20% and 40% aqueous (v/v) dioxane. Although at the present time there is no direct evidence

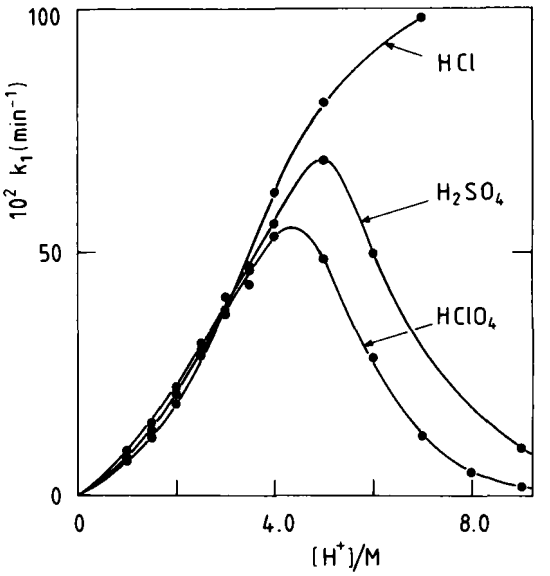
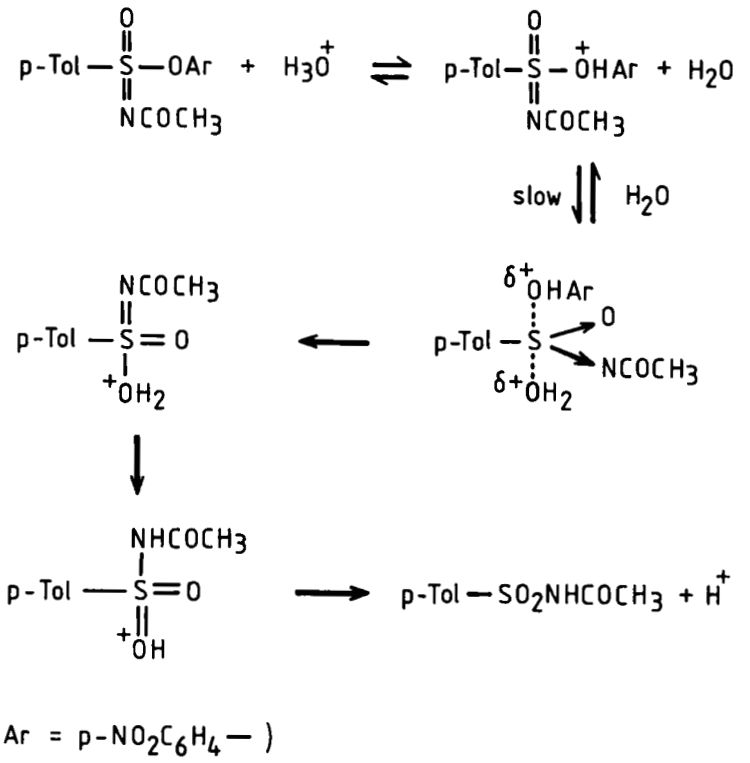



FIGURE 1 Plots of $k_1$ for acid-catalysed hydrolysis of **1b** in aqueous 40% (v/v) dioxane at 25.0°C.




(Ar = p-$NO_2C_6H_4$— )

Scheme 1

for the site of protonation of **1a** or **1b**, a possible mechanistic scheme for the hydrolysis of **1b** which involves protonation on oxygen is shown in Scheme 1.

Values of $k_1$ for the perchloric acid catalysed hydrolyses of N-aroylsulphonimidic esters **2** (**a**–**e**) in aqueous 40% (v/v) dioxane are shown in Figure 2. In all cases the rates of hydrolyses increase continuously with increasing concentration of acid and then is no indication of a rate maximum even at quite high acidity. The order of catalytic effectiveness of acids observed for the hydrolyses of 2(a–d) was $HClO_4$ > $H_2SO_4$ > HCl and is shown in Table I and Figure 3 for **2a**. Bunton and his co-workers have suggested that such an order is characteristic of a dissociative mechanism, transition states of positive character being preferentially stabilised by anions of low charge density such as $ClO_4^-$, whereas the converse is usually the case for A-2 reactions.[4]

The kinetic data in Figure 2 were also analysed by the Excess Acidity treatment of Cox and Yates.[5] A simplified version of their relationship for mainly unprotonated substrates [Equation (1)] was used. Due to the extremely low basicity of the sulphonimidic esters studied, the

$$\log k_1 - \log[H^+] - \log c_S/(c_S + c_{SH^+}) = m^*m\ddagger X + \log a_{Nu} + \log(k_0/k_{SH^+}) \quad (1)$$

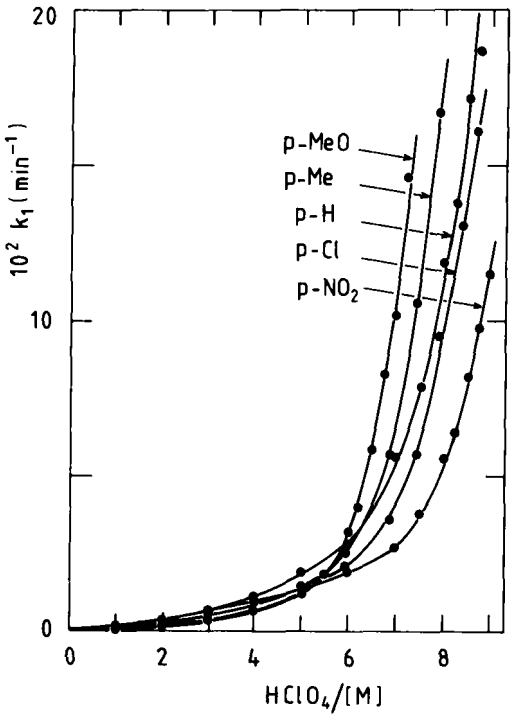



FIGURE 2 Plots of $k_1$ for perchloric acid-catalysed hydrolysis of **2a–e** in aqueous 40% (v/v) dioxane at 50.0°C.

TABLE I

Values of $10^2$ $k_1$ (min$^{-1}$) for the hydrolyses of sulphonimidic esters in aqueous (40% v/v) dioxane at 50.0°C

| [H$^+$]/M | 1.00 | 2.00 | 3.00 | 4.00 | 5.00 | 6.00 |
|---|---|---|---|---|---|---|
| **2c** $H_2SO_4$ | 0.116 | 0.281 | 0.492 | 0.882 | 1.60 | 2.70 |
| **2c** HCl | 0.064 | 0.188 | 0.376 | 0.723 | 1.23 | 1.90 |
| **2b** $H_2SO_4$ | 0.062 | 0.145 | 0.366 | 0.726 | 1.202 | 1.70 |
| **2b** HCl | 0.053 | 0.142 | 0.284 | 0.515 | 0.959 | 1.40 |
| **2e** $H_2SO_4$ | 0.093 | 0.19 | 0.33 | 0.54 | 0.97 | 1.53 |
| **2e** HCl | 0.067 | 0.121 | 0.24 | 0.43 | 0.659 | 1.03 |
| [H$^+$]/M | 6.50 | 7.00 | 7.50 | 8.00 | 9.00 | 10.00 |
| **2c** $H_2SO_4$ | — | 4.81 | — | 8.69 | 14.4 | — |
| **2c** HCl | — | 2.56 | — | 4.34 | — | — |
| **2b** $H_2SO_4$ | — | 2.74 | — | 7.56 | 16.5 | 26.3 |
| **2b** HCl | — | 2.33 | — | 3.75 | — | — |
| **2e** $H_2SO_4$ | 2.22 | 2.84 | 4.6 | 5.93 | — | — |
| **2e** HCl | — | 1.94 | — | 2.89 | — | — |

protonation correction term can be neglected. Values of $X$ for aqueous solutions of acid were used in the absence of such values for aqueous organic solvents.[6]

A plot of log $k_1$ − log[H$^+$] versus $X$ is shown in Figure 4 for hydrolysis of **2c** (R = H) in sulfuric acid. Such graphs for the sulphonimidic esters all initially, in the low acidity region, exhibit downward curvature typical of A-2 reactions in-

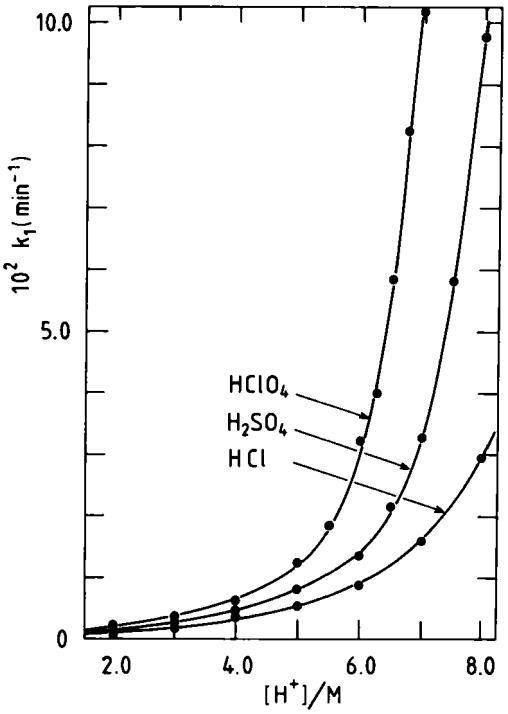



FIGURE 3 Plots of $k_1$ for acid-catalysed hydrolysis of **2a** in aqueous 40% (v/v) dioxane at 50.0°C.

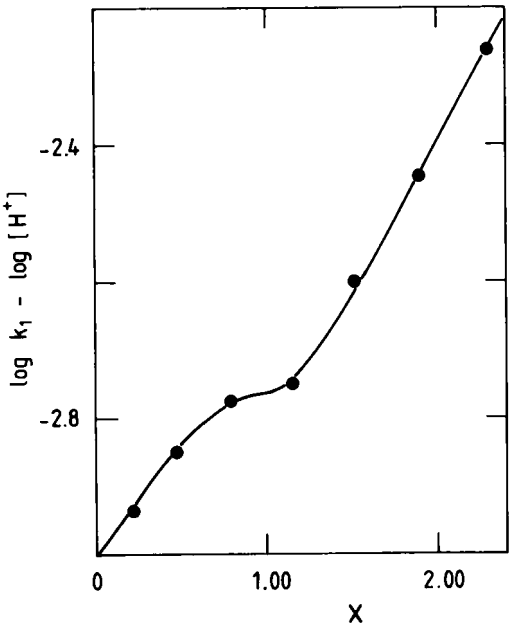



FIGURE 4 Plot of log $k_1$ − log[H$^+$] vs. excess acidity for the sulphuric acid-catalysed hydrolysis of **2c** in aqueous 40% (v/v) dioxane at 50.0°C.

TABLE II

Deuterium solvent isotope effect for hydrolysis of 2c in aqueous 40% (v/v) dioxane

| T°C | Acid | $k_1D_2O/k_1H_2O$ |
|---|---|---|
| 48.0 | $H_2SO_4$ – 3.00M | 1.46 |
| 40.0 | $HClO_4$ – 3.00M | 1.63 |
| 30.0 | $HClO_4$ – 7.50M | 1.95 |

TABLE III

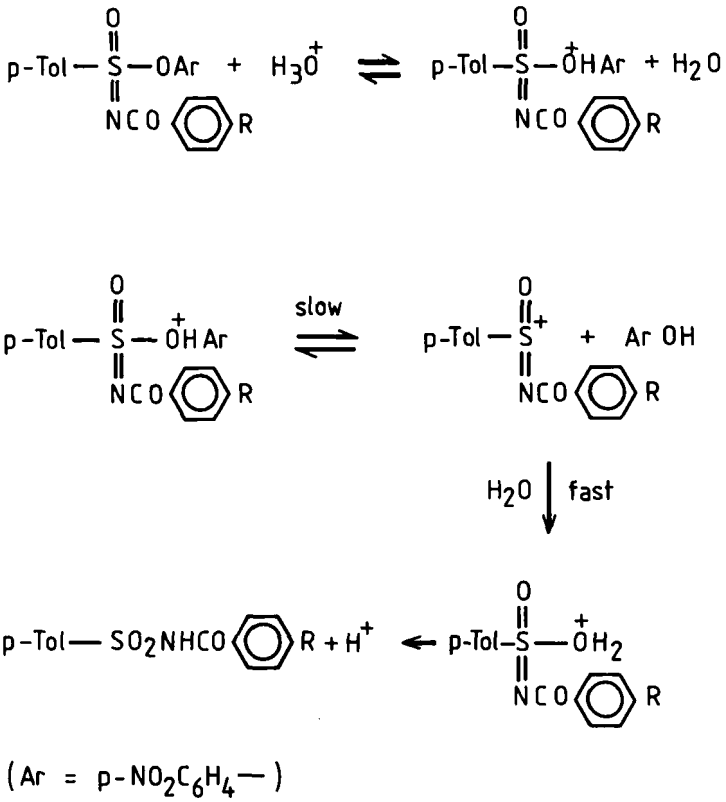
Arrhenius parameters for hydrolysis of sulphonimidic esters in aqueous 40% (v/v) dioxane

| Ester | Acid | $[H^+]$/M | ΔH‡ | ΔS‡ |
|---|---|---|---|---|
| **1b** | $HClO_4$ | 2.00 | 14.4 | −13.1 |
| | $H_2SO_4$ | 2.00 | 14.0 | −14.7 |
| | HCl | 2.00 | 14.0 | −15.1 |
| **2a** | $HClO_4$ | 3.00 | 20.8 | −5.6 |
| | | 6.50 | 24.2 | +10.5 |
| | HCl | 3.00 | 18.6 | −14.0 |
| | | 8.00 | 20.1 | −3.5 |
| **2c** | $HClO_4$ | 3.00 | 20.1 | −6.31 |
| | | 5.00 | 20.0 | −4.60 |
| | | 6.00 | 21.2 | −0.28 |
| | | 7.50 | 22.9 | +7.15 |
| | | 8.50 | 23.2 | +9.73 |
| | $H_2SO_4$ | 3.00 | 18.9 | −10.8 |
| | | 8.00 | 18.2 | −7.4 |
| | | 12.00 | 22.1 | +7.3 |
| | HCl | 3.00 | 16.8 | −17.8 |
| | | 8.00 | 18.6 | −7.5 |
| **2e** | $HClO_4$ | 3.00 | 19.9 | −7.6 |
| | | 8.00 | 23.4 | +7.8 |
| | HCl | 3.00 | 16.9 | −18.5 |
| | | 8.00 | 18.7 | −7.9 |



volving water.[7] This changes with increasing acidity to an upward linear region characteristic of an A-1 process. Similar behaviour has been observed for the hydrolyses of a number of esters and related compounds.[8,9] This suggests that a gradual changeover in mechanism from A-2 to A-1 occurs with increasing concentration of acid.

Such a changeover is supported by the changes which occur in the entropies of activation for the hydrolyses of **2a**, **2c**, and **2e** as shown in Table III. Over the range 3.0–8.0 M perchloric acid the values of ΔS‡ change from −6.3 to +9.7 and −7.6 to +7.8 cal.deg$^{-1}$mol$^{-1}$ for the hydrolyses of **2c** (R = H) and **2e** (R = $NO_2$), respectively. Values in sulphuric acid vary in a similar way while, as expected, those in hydrochloric acid remain much more negative. The increasing values with acidity of the kinetic solvent isotope effect (e.g., for **2c** (R = H); $k_1D_2O/k_1H_2O$ = 1.63 (3.00 M $[H^+]$ and 1.95 (7.50 M $[H^+]$) (Table II) are also consistent with a change from A-2 to A-1.[10] We propose therefore that the acid-catalysed hydrolysis of N-aroylsulphonimidic esters in 40% v/v aqueous dioxane occurs at low acidity by the A-2 mechanism proposed above for the hydrolysis in both 20% and 40% aqueous dioxane of N-acetylsulphonimidic esters and that there is a progressive change with increasing acidity to an A-1 dissociative mechanism (Scheme 2). This changeover occurs at much lower acidity for hydrolysis in perchloric and sulphuric




Scheme 2

acids than in hydrochloric acid. At acidities higher than 6.0 Molar [$H^+$], electron-donating substituents produce the highest rate of hydrolysis [i.e., **2a** > **2e**] and the substituent effects are well correlated by a satisfactory Hammett $\sigma\rho$ plot [at 7.00 M $HClO_4$, $\rho$ = 0.57 (corr. 0.998)]. Clearly at these acidities electron-donating substituents facilitate both protonation of the substrate and stabilise the sulphur cation of the A-1 mechanism. At lower acidities, however, (e.g., 3.0 M-$HClO_4$), **2e** hydrolyses more rapidly than **2a** consistent with a predominantly A-2 mechanism in which substituent effects on the protonation and slow step operate in opposite directions.

TABLE IV

Analytical Data for p-nitrophenyl esters of N-acyl-p-tolueneiminosulphonic acids

| | | Expected % | | | | Molecular formula | Found % | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | M.P.°C | C | H | N | S | | C | H | N | S |
| **1b** | 87 | 53.9 | 4.2 | 8.4 | 9.6 | $C_{15}H_{14}N_2O_5S$ | 53.9 | 4.3 | 8.3 | 9.7 |
| **2a** | 117–118 | 59.1 | 4.3 | 6.6 | 7.5 | $C_{21}H_{18}N_2O_6S$ | 59.2 | 4.4 | 6.6 | 7.8 |
| **2b** | 146–147 | 61.4 | 4.4 | 6.8 | 7.8 | $C_{21}H_{18}N_2O_5S$ | 61.5 | 4.5 | 6.8 | 7.6 |
| **2d** | 169–170 | 55.7 | 3.5 | 6.5 | 8.2 | $C_{20}H_{15}N_2O_5SCl$ | 55.2 | 3.4 | 6.5 | 8.2 |
| **2e** | 183 | 54.4 | 3.4 | 9.5 | 7.3 | $C_{20}H_{15}N_3O_7S$ | 54.4 | 3.5 | 9.6 | 7.1 |

## EXPERIMENTAL

*Materials.* Sulphonimidic esters (**1b, 2**) were prepared from the corresponding N-acyl iminosulphonyl chlorides which were synthesized following the procedure of Levchenko and her co-workers[11-13] as described previously.[1] This involved reaction of p-toluenesulphonyl chloride with the appropriate N-chloramide in the presence of pyridine to give the iminosulphonyl chloride followed by reaction with sodium p-nitrophenoxide in benzene. The N-chloroamides[14,15] and p-nitrophenyl N-benzoyl-p-tolueneiminosulphonate[1] were prepared as described in the literature. Analytical data for novel esters are shown in Table IV.

*Kinetic Procedure.* The rates of hydrolysis of sulphonimidic esters were followed spectrophotometrically at 315–320 nm using a Perkin Elmer model 554 spectrometer with a thermostatted cell compartment (±0.05°C). Good first-order behaviour was observed with clean isosbestic points. 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 were shown to be identical to that of an equivalent mixture of p-nitrophenol and the corresponding N-acetyl or N-aroyl-p-toluenesulphonamides.

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