# THE ACID — CATALYSED HYDROLYSIS OF SULPHINATE ESTERS

AZHARI SALLEH,
*Jabatan Kimia,*
*Universiti Teknologi Malaysia,*
*Kuala Lumpur.*

## RINGKASAN

*Hidrolisis berbagai ester sulfinat dalam larutan berair asid galian telah dikaji secara kinetik. Analisis data kinetik yang diperolehi mengikut kaedah Bunnett dan Bunnett-Olsen dan entropi keaktifan menunjukkan bahawa hidrolisis berlaku mengikut mekanisma A–2.*

## ABSTRACT

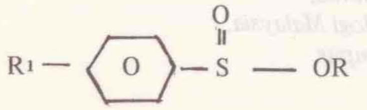
The hydrolysis of substituted sulphinate esters in aqueous mineral acids have been kinetically studied. Analysis of the kinetic data by Bunnett and Bunnett-Olsen criteria and by entropy of activation suggest that the hydrolysis proceed with an A-2 mechanism.

## Introduction

Sulphinic acids are comparatively weak[1] (pKa = 2) and one might expect that the hydrolysis of their esters would be different from those of alkyl suphonates, which undergo hydrolysis via C–0 bond fission in both acidic and alkaline media[2]. The hydrolysis of methyl p-toluenesulphinate in acidic $H_2{}^{18}O$ – dioxane proceeds with S–O bond fission[3]. Bunton and Hendy[3,4] showed that the perchloric acid catalysed hydrolysis of methyl p-toluenesulphinate proceeded with an A–2 reaction mechanism. However, with halogen acids as catalysts, the hydrolysis proceeds concurrently via an A–2 and a hydrogen ion dependent nucleophilic catalysis mechanism.

The acid-catalysed hydrolysis of diphenylmethyl p-toluenesulphinate on the other hand shows quite complex kinetic behaviour [5]. Perchloric acid is a particulary effective catalyst, and based on kinetic studies an A–1 mechanism has been suggested for the perchloric acid-catalysed hydrolysis of diphenylmethyl p-toluenesulphinate. Tracer experiments with $H_2{}^{18}O$, however shows that the hydrolysis proceeds with 80% C–0 and 20% S–0 bond fission. This indicates that concurrent displacement of both carbon and sulphur occurs.

I now report a kinetic study of acid catalysed hydrolysis of substituted sulphinate esters. A number of substituted sulphinate esters (I;



I

where

$R^1$ = $CH_3$ ; R = $CH_3$, $C_6H_5CH_2$ and i – $C_3H_7$

and

R = $CH_3$ ; $R^1$ = Cl and H) have been prepared.

## EXPERIMENTAL

Materials: The sulphinate esters were prepared by the addition of suphinyl chloride to the appropriate alcohol in pyridine according to the method described by Wragg and coworkers [6]. Methyl p-toluenesulphinate had b.p. 90 – 94° C/0.6 mm (lit [6] b.p. 129 – 130 ° C/14 mm). (Found: C, 56.7%; H, 5.8%; S, 18.9%. $C_8H_{10}SO_2$ required C, 56.5%; H, 5.9%, S, 18.8). NMR δ ($CCl_4$) 7.25 – 6.80 (2d, 4H), 2.97 (s, 3H) and 1.93 (s, 3H). Benzyl p-toluenesulphinate had m.p. 22 – 23 ° C (Lit [6] .m.p. 22 – 24 ° C). (Found: C, 68.1%; H, 5.8%, S, 13.1%, $C_{12}H_{14}SO_2$ required C, 68.3%; H, 5.7%; S, 13.0%) NMR δ ($CCl_4$) 7.77 – 7.33 (m, 9H), 5.17 – 4.47 (m, 2H) and 2.45 (s, 3H). Isopropyl p-toluenesulphinate had b.p. 84 – 86 ° C/0.25m. (Found: C, 60.6%; H, 7.2%; S, 15.8%; $C_{10}H_{14}SO_2$ required C, 60.6%; H, 7.1%; S, 16.2%, NMR δ ($CCl_4$) 7.31 – 6.81 (2d, 4H), 4.35 – 3.95 (m, 1H), 1.95 (s, 3H) and 0.98 – 0.70 (2d, 6H). Methyl benzenesulphinate had b.p. 60 – 62° C/0.3 mm (lit [6] b.p. 76 – 81° C/0.45 mm). (Found: C, 53.8%; H, 5.0%; S, 20.5%; $C_7H_8SO_2$ required C, 53.9%; H. 5.1%, S, 20.5%). NMR δ ($CCl_4$) 7.12 (m, 5H) and 2.90 (s, 3H) and methyl p-chlorobenzenesulphinate had b.p. 91 – 92° C/0.5 mm. (Found: C, 43.9%, H, 3.7%; S, 16.8% $C_7H_7ClSO_2$ required C, 44.1%; H, 3.7%; S, 16.8%). NMR δ ($CCl_4$) 7.45 – 7.10 (2d, 4H) and 3.13 (s, 3H).

Kinetic Measurements: The rates of hydrolysis were determined spectrophotometrically by following the decrease in the characteristic absorption of sulphinates at wavelengths between 235 – 245 nm with a Unicam Sp 800 spectrometer equipped with a slave recorder and thermostatted cell compartment (± 0.05 ° C). Values of the first-order rate coefficents k ψ were calculated for each run from standard equation and are shown in Tables 1 – 5.

The concentration of sulphinate esters used was ca. $10^{-4}$ M.

## TABLE I

Hydrolysis of Methyl p-toluenesulphinate

(a) Effect of added acids at 25.20 ° C.

| | | | | | | |
|---|---|---|---|---|---|---|
| $(HC10_4)/M$ | 0.50 | 1.00 | 1.00* | 1.50 | 2.00 | 2.50 |
| $10^4 k_\psi/sec^{-1}$ | 0.345 | 0.742 | 1.51 | 1.06 | 1.65 | 1.74 |
| $(HC10_4)/M$ | 3.00 | 3.50 | 4.00 | 4.50 | 5.00 | 5.20 |
| $10^4 k_\psi/sec^{-1}$ | 2.13 | 2.73 | 3.76 | 5.95 | 7.45 | 11.7 |
| $(HC10_4)/M$ | 6.00 | 6.50 | 7.00 | 7.50 | | |
| $10^4 k_\psi/sec^{-1}$ | 14.2 | 25.2 | 34.8 | 65.8 | | |
| $(H_2SO_4)/M$ | 0.50 | 1.00 | 1.50 | 2.00 | 2.50 | 3.00 |
| $10^4 k_\psi/sec^{-1}$ | 0.436 | 0.951 | 2.21 | 3.42 | 7.63 | 10.4 |
| $(H_2SO_4)/M$ | 3.50 | 4.00 | 4.50 | 5.00 | 6.00 | 7.00 |
| $10^4 k_\psi/sec^{-1}$ | 14.8 | 21.7 | 30.5 | 43.5 | 85.8 | 208 |
| $(HC1)/M$ | 0.50 | 1.00 | 1.50 | 2.00 | 2.50 | 3.00 |
| $10^4 k_\psi/sec^{-1}$ | 0.910 | 5.73 | 14.8 | 25.4 | 44.9 | 80.9 |

* In 99.8% $DC\ell O_4 - D_2O$

(b) Effect of perchloric acid (2.00M) at different temperatures.

| | | | | | |
|---|---|---|---|---|---|
| T/°C | 25.2 | 30.2 | 35.0 | 39.4 | 44.3 |
| $10^4 k_\psi/sec^{-1}$ | 1.65 | 2.36 | 4.32 | 7.10 | 12.0 |

(c) Effect of perchloric acid (7.00M) at different temperatures.

| | | | | | |
|---|---|---|---|---|---|
| T/°C | 20.4 | 25.2 | 30.2 | 35.0 | 39.4 |
| $10^4 k_\psi/sec^{-1}$ | 23.2 | 34.8 | 69.6 | 120 | 190 |

(d) Effect of sulphuric acid (2.00M) at different temperatures.

| | | | | | |
|---|---|---|---|---|---|
| T/°C | 25.2 | 30.2 | 35.0 | 39.4 | 44.3 |
| $10^4 k_\psi/sec^{-1}$ | 3.42 | 6.16 | 11.9 | 16.2 | 24.2 |

## TABLE 2

Hydrolysis of Benzyl p-toluenesulphinate

(a) Effect of added acids at 25.10°C.

| | | | | | | |
|---|---|---|---|---|---|---|
| $(HC10_4)/M$ | 0.50 | 1.00 | 1.50 | 2.00 | 2.50 | 3.00 |
| $10^4 k_\psi/sec^{-1}$ | 0.420 | 0.733 | 1.67 | 2.18 | 2.92 | 4.05 |
| $(HC10_4)/M$ | 3.50 | 4.00 | 4.50 | 5.00 | 6.00 | 1.00* |
| $10^4 k_\psi/sec^{-1}$ | 5.43 | 7.21 | 9.67 | 13.2 | 22.0 | 1.44 |
| $(H_2SO_4)/M$ | 0.50 | 1.00 | 1.50 | 2.00 | 2.50 | 3.00 |
| $10^4 k_\psi/sec^{-1}$ | 0.644 | 1.58 | 3.06 | 4.98 | 9.20 | 13.1 |
| $(H_2SO_4)/M$ | 3.50 | 4.00 | 4.50 | 5.00 | 6.00 | |
| $10^4 k_\psi/sec^{-1}$ | 18.9 | 34.3 | 48.8 | 78.8 | 165 | |

* In 99.8% $DC10_4 - D_2O$

(b) Effect of perchloric acid (2.00M) at different temperatures

| | | | | | |
|---|---|---|---|---|---|
| T/°C | 20.4 | 25.1 | 29.7 | 34.1 | 38.6 |
| $10^4 k_\psi/sec^{-1}$ | 1.27 | 2.18 | 3.40 | 5.54 | 9.04 |

(c) Effect of sulphuric acid (2.00M) at different temperatures.

| | | | | | |
|---|---|---|---|---|---|
| T/°C | 20.4 | 25.1 | 29.7 | 34.1 | 38.6 |
| $10^4 k_\psi/sec^{-1}$ | 2.92 | 4.98 | 9.30 | 12.5 | 19.4 |

(d) Effect of sulphuric acid (5.00M) at different temperatures

| | | | | | |
|---|---|---|---|---|---|
| T/°C | 20.4 | 25.1 | 29.7 | 34.1 | 38.6 |
| $10^4 k_\psi/sec^{-1}$ | 49.0 | 79.0 | 124 | 186 | 266 |

(e) Effect of perchloric acid (6.00M) at different temperatures

| | | | | | |
|---|---|---|---|---|---|
| T/°C | 20.4 | 25.1 | 29.7 | 34.1 | 38.6 |
| $10^4 k_\psi/sec^{-1}$ | 12.8 | 22.0 | 37.4 | 60.1 | 102 |

## TABLE 3

Hydrolysis of Isopropyl p-toluenesulphinate

(a) Effect of added acids at 25.30° C.

| | | | | | | |
|---|---|---|---|---|---|---|
| $(HC10_4)/M$ | 0.50 | 1.00 | 1.50 | 2.00 | 2.50 | 3.00 |
| $10^4 k_\psi/sec^{-1}$ | 0.150 | 0.308 | 0.502 | 0.959 | 1.15 | 1.48 |
| $(HC10_4)/M$ | 3.50 | 4.00 | 4.50 | 5.00 | 5.50 | 6.00 |
| $10^4 k_\psi/sec^{-1}$ | 1.82 | 2.29 | 2.75 | 3.29 | 5.59 | 6.35 |
| (HC10)/M | 6.50 | 7.00 | 7.50 | 8.00 | | |
| $10^4 k_\psi/sec^{-1}$ | 10.8 | 14.4 | 34.0 | 38.4 | | |
| $(H_2SO_4)/M$ | 0.50 | 1.00 | 1.00* | 1.50 | 2.00 | 2.50 |
| $10^4 k_\psi/sec^{-1}$ | 0.262 | 0.566 | 1.26 | 1.15 | 2.11 | 3.97 |
| $(H_2SO_4)/M$ | 3.00 | 3.50 | 4.00 | 4.50 | 5.00 | 6.00 |
| $10^4 k_\psi/sec^{-1}$ | 5.87 | 10.2 | 14.5 | 16.8 | 20.5 | 45.7 |

* In $D_2SO_4 + D_2O$

(b) Effect of perchloric acid (2.00M) at different temperatures

| | | | | | |
|---|---|---|---|---|---|
| T/°C | 20.3 | 25.3 | 29.1 | 33.9 | 38.6 |
| $10^4 k_\psi/sec^{-1}$ | 0.526 | 0.96 | 1.28 | 2.24 | 3.64 |

(c) Effect of sulphuric acid (2.00M) at different temperatures.

| T/ °C | 20.3 | 25.3 | 29.1 | 33.9 | 38.6 |
|---|---|---|---|---|---|
| $10^4 k_\psi$/sec$^{-1}$ | 1.26 | 2.12 | 2.96 | 5.23 | 8.23 |

## TABLE 4

Hydrolysis of Methyl benzenesulphinate

(a) Effect of added acids at 25.30°C.

| | | | | | | |
|---|---|---|---|---|---|---|
| $(HC10_4)$/M | 0.50 | 1.00 | 1.00* | 1.50 | 2.00 | 2.50 |
| $10^4 k_\psi$/sec$^{-1}$ | 0.227 | 0.312 | 0.615 | 0.629 | 0.976 | 1.22 |
| $(HC10_4)$/M | 3.00 | 3.50 | 4.00 | 4.50 | 5.00 | 5.50 |
| $10^4 k_\psi$/sec$^{-1}$ | 1.45 | 1.74 | 2.16 | 3.21 | 4.07 | 5.61 |
| $(HC10_4)$/M | 6.00 | 6.50 | 7.00 | 7.50 | | |
| $10^4 k_\psi$/sec$^{-1}$ | 6.28 | 9.92 | 11.3 | 16.2 | | |
| $(H_2SO_4)$/M | 0.50 | 1.00 | 1.50 | 2.00 | 2.50 | 3.00 |
| $10^4 k_\psi$/sec$^{-1}$ | 0.318 | 0.933 | 1.46 | 2.46 | 4.57 | 6.29 |
| $(H_2SO_4)$/M | 3.50 | 4.00 | 4.50 | 5.00 | 5.50 | 6.00 |
| $10^4 k_\psi$/sec$^{-1}$ | 9.19 | 13.1 | 19.9 | 25.4 | 38.4 | 53.5 |

(b) Effect of perchloric acid (2.00M) at different temperatures.

| T/°C | 20.4 | 25.3 | 29.3 | 33.8 | 38.4 |
|---|---|---|---|---|---|
| $10^4 k_\psi$/sec$^{-1}$ | 0.464 | 0.976 | 1.68 | 2.22 | 4.54 |

(c) Effect of perchloric acid (5.00M) at different temperatures.

| T/°C | 20.4 | 25.3 | 29.3 | 33.8 | 38.4 |
|---|---|---|---|---|---|
| $10^4 k_\psi$/sec$^{-1}$ | 2.04 | 4.07 | 6.20 | 9.40 | 15.2 |

(d) Effect of sulphuric acid (2.00M) at different temperatures.

| T/ °C | 20.4 | 25.3 | 29.3 | 33.8 | 38.4 |
|---|---|---|---|---|---|
| $10^4 k_\psi$/sec$^{-1}$ | 1.53 | 2.46 | 3.68 | 6.36 | 10.5 |

(e) Effect of sulphuric acid (5.00M) at different temperatures.

| T/ °C | 20.4 | 25.3 | 29.3 | 33.8 | 38.4 |
|---|---|---|---|---|---|
| $10^4 k_\psi$/sec$^{-1}$ | 14.8 | 25.4 | 35.7 | 56.0 | 88.0 |

## TABLE 5

Hydrolysis of Methyl p-chlorobenzenesulphinate

(a) Effect of added acids at 25.30° C.

| | | | | | | |
|---|---|---|---|---|---|---|
| $(HC10_4)$/M | 0.50 | 1.00 | 1.50 | 2.00 | 2.50 | 3.00 |
| $10^4 k_\psi$/sec$^{-1}$ | 0.122 | 0.249 | 0.367 | 0.506 | 0.586 | 0.954 |
| $(HC10_4)$/M | 3.50 | 4.00 | 4.50 | 5.00 | 5.50 | 6.00 |
| $10^4 k_\psi$/sec$^{-1}$ | 1.08 | 1.21 | 1.74 | 2.15 | 3.04 | 3.41 |
| $(HC10_4)$/M | 6.50 | 7.00 | 7.50 | 8.00 | | |
| $10^4 k_\psi$/sec$^{-1}$ | 5.38 | 6.70 | 9.02 | 10.0 | | |
| $(H_2SO_4)$/M | 0.50 | 1.00 | 1.50 | 2.00 | 2.50 | 3.00 |
| $10^4 k_\psi$/sec$^{-1}$ | 0.231 | 0.571 | 1.09 | 1.66 | 2.25 | 3.32 |
| $(H_2SO_4)$/M | 3.50 | 4.00 | 4.50 | 5.00 | 6.00 | 7.00 |
| $10^4 k_\psi$/sec$^{-1}$ | 7.00 | 9.30 | 16.7 | 19.7 | 34.2 | 63.5 |

(b) Effect of perchloric acid (2.00M) at different temperatures.

| T/ °C | 20.7 | 25.3 | 29.9 | 34.3 | 38.7 |
|---|---|---|---|---|---|
| $10^4 k_\psi$/sec$^{-1}$ | 0.298 | 0.506 | 0.840 | 1.33 | 2.12 |

(c) Effect of sulphuric acid (2.00M) at different temperatures.

| T/ °C | 20.7 | 25.3 | 29.9 | 34.3 | 28.7 |
|---|---|---|---|---|---|
| $10^4 k_\psi$/sec$^{-1}$ | 0950 | 1.66 | 2.72 | 4.16 | 6.26 |

**Influence of Temperature**: The entropy ( $\Delta S\ddagger$ ) and enthalpy of activation ( $\Delta H\ddagger$ ) were calculated from the equation $k = (kT/h)\ \exp\ (\Delta S\ddagger/R)\ \exp\ (\Delta H\ddagger/RT)$ by a least-squares procedure. The calculated values are shown in Table 6.

## TABLE 6

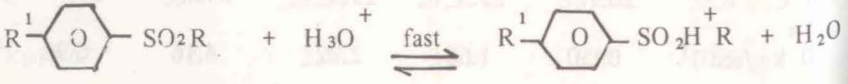
Values of $\Delta H\ddagger$ and $\Delta S\ddagger$ for the hydrolysis of substituted sulphinate esters at 25.0 ℃.

| Sulphinate esters | Catalyst | $\Delta H\ddagger$ (KJ mol$^{-1}$) | $-\Delta S\ddagger$ (JK$^{-1}$ mol$^{-1}$) |
|---|---|---|---|
| Methyl p-toluene-sulphinate | 2.00M–HC10$_4$ | 81.5 ± 4.6 | 51.7 ± 14.7 |
| | 7.00M–HC10$_4$ | 84.4 ± 3.4 | 25.3 ± 10.7 |
| | 2.00M–$H_2SO_4$ | 80.6 ± 4.5 | 47.8 ± 14.3 |
| Methyl p-chloro-benzenesulphinate | 2.00M–HC10$_4$ | 81.3 ± 0.9 | 61.9 ± 3.1 |
| | 2.00M–$H_2SO_4$ | 77.2 ± 1.8 | 65.7 ± 6.0 |
| Methyl benzene-sulphinate | 2.00M–HC10$_4$ | 89.9 ± 6.5 | 27.8 ± 21.4 |
| | 5.00M–HC10$_4$ | 80.8 ± 3.5 | 54.2 ± 11.2 |
| | 2.00M–$H_2SO_4$ | 79.8 ± 2.8 | 53.3 ± 9.2 |
| | 5.00M–$H_2SO_4$ | 72.2 ± 1.3 | 67.6 ± 4.4 |
| Isopropyl p-toluene-sulphinate | 2.00M–HC10$_4$ | 77.9 ± 2.0 | 68.2 ± 6.5 |
| | 2.00M–$H_2SO_4$ | 76.7 ± 2.2 | 65.2 ± 7.4 |
| Benzyl p-toluene-sulphinate | 2.00M–HC10$_4$ | 79.3 ± 1.4 | 56.3 ± 4.6 |
| | 6.00M–HC10$_4$ | 84.7 ± 0.8 | 27.6 ± 2.6 |
| | 2.00M–$H_2SO_4$ | 77.0 ± 1.3 | 56.8 ± 4.2 |
| | 5.00M–$H_2SO_4$ | 68.9 ± 1.3 | 68.6 ± 4.2 |

## DISCUSSION

The kinetic behaviour observed for the acid-catalysed hydrolysis of sulphinate esters of methyl p-toluene-, methyl p-chlorobenzene-, methyl benzene-, isopropyl p-toluene- and benzyl p-toluenesulphinates is so similar that the following discussion could be taken from the data of either compound.

The Proton Transfer: The values obtained for the deuterium kinetic solvent isotope effect ($k_{D_2O}/k_{H_2O}$) for the perchloric and sulphuric acid catalysed hydrolysis of sulphinate esters lie in the range 1.96 – 2.23 and are characteristic of reactions which proceed by preequilibrium proton transfer, i.e. specific hydrogen ion catalysis occurs.



Rate Dependence on Acidity: The rates of hydrolysis of all sulphinate esters studied, at first, increase linearly with acid concentration, but above ca. 2.00M the rate increases more rapidly than the increase in acid concentration (Table 1 – 5). This is probably due to a positive salt effect superimposed on a linear dependence of rate on stiochiometric acid concentration. Such behaviour is characteristic of many reactions which hydrolyse by an A–2 mechanism, e.g. the acid-catalysed hydrolysis of ethyl acetate[8], methyl phosphate[9] and dialkylsulphites[10-11].

Table 7 summarises the analysis of the hydrolysis rate of sulphinate esters by the use of Bunnett w and w* parameters and Bunnett-Olsen linear free energy relationship. Bunnett's earlier proposal[12] for the classification of reactions in strong acid media involves a plot of log $k\psi + H_o$ verses log $a_{H_2O}$. Such plots of the hydrolysis of sulphinate esters studied give a good linear correlation with values of w (1.45 – 2.40) which fall into the range associated with water acting as a nucleophile. Bunnett w* plot of log $k\psi - \log [H^+]$ against log $a_{H_2O}$ also gives a good straight line with values of w* (–2.10 → –4.18) in the range associated with water acting as nucleophile. The Bunnett–Olsen linear free energy relationship approach[13] involves a plot of ($\log k\psi + H_o$) against ($H_o + \log (H^+)$ ] to give a slope parameter, $\phi$ Such plots again give a good straight line for the hydrolysis of sulphinate esters with values that lie in the range 0.28 – 0.47 characteristic of reaction proceeds with an A–2 mechanism with water acting as nucleophile.

## TABLE 7

Values of the Bunnett and Bunnett–Olsen Parameters for the hydrolysis of sulphinate esters in $H_2SO_4$ at 25.0°C.

| Sulphinate Ester | W Value | W* Value | $\Phi$ Value |
|---|---|---|---|
| Methyl p-toluene-sulphinate | 1.71 (0.9995) | – 2.61 (0.998) | 0.44 (0.9995) |
| Methyl p-chloro-benzenesulphinate | 2.40 (0.9997) | – 2.70 (0.998) | 0.57 (0.996) |
| Methyl benzene-sulphinate | 1.84 (0.997) | – 2.70 (0.995) | 0.40 (0.998) |
| Isopropyl p-toluene-sulphinate | 1.45 (0.997) | – 2.42 (0.998) | 0.47 (0.993) |
| Benzyl p-toluene-sulphinate | 1.45 (0.995) | – 4.18 (0.992) | 0.28 (0.996) |

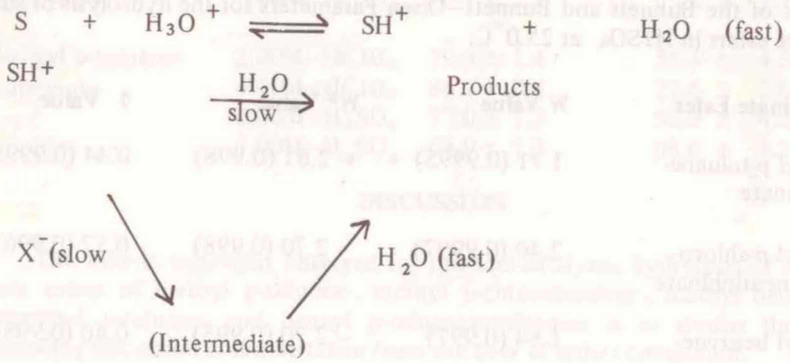
* linear correlation coefficient in parenthesis.

Another criterion of mechanism which can be used to differentiate between an A–1 and A–2 pathways is the value of entropy of activation. Typically a rather more positive entropy of activation would be expected for a unimolecular reaction, whereas the corresponding bimolecular reaction will show a relatively large negative entropy because of the loss of transitional and rotational freedom of water molecules [14]. All values of $\Delta S^{\ddagger}$ listed in Table 6 for the hydrolysis of sulphinate esters show a relatively large negative which can be associated with an A–2 type of mechanism.

Nucleophililic catalysis: The order of effectiveness of catalysing acids $HCI > H_2SO_4 > HC10_4$ for the hydrolysis of methyl p-toluenesulphinate (Table 1) and the magnitude of the relative effects suggests the occurance of nucleophilic catalysis. Bunton and Hendy [4] observed that added salts increase the rate of acid catalysis, sodium chloride being much more effective than sodium perchloriate. This suggests that the observed rate coefficient for the hydrolysis of sulphinate esters consists of two terms which in an A–2 reaction and a hydrogen ion dependent nucleophilic catalysis respectively as represented in equation.

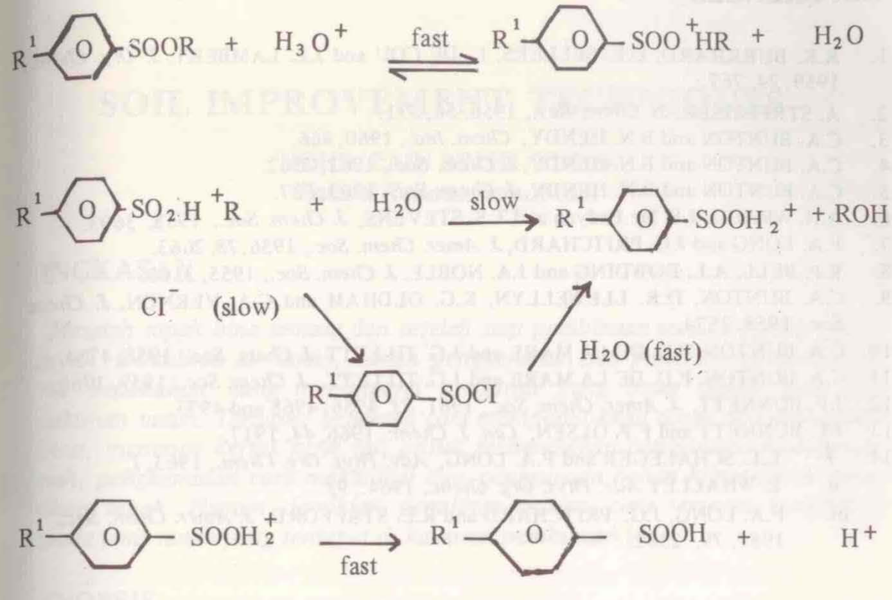
$$k = k_{H+}[H^+] + k_{X^-}[H^+][X^-]$$

A general scheme for the hydrolysis of sulphinate esters study therefore may be represented as scheme 1.



**Scheme I**

The overall possible mechanism for the hydrolysis of sulphinate esters with halogen acids which proceed concurrently via an A–2 and hydrogen ion dependent nucleophilic catalysis can be represented as in scheme 11.



**Scheme II**

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