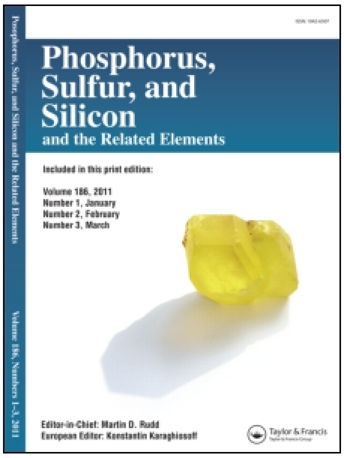

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ACID-CATALYSED HYDROLYSIS OF SOME AROMATIC CYCLIC SULFAMATES

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*The acid catalysed hydrolysis of some cyclic sulfamates, X-3-(p-tolylsulfonyl)-1,2,3-benzoxathiazole 2,2-dioxides (**1a**, X = Me; **1b**, X = H; **1c**, X = Cl; **1d**, X = NO_2) have been studied in concentrated aqueous sulfuric and perchloric acid solutions. Analysis of the data by the Excess Acidity Method, activation parameters, substituent, solvent deuterium isotope effect and order of the catalytic effects of the acids are all in agreement with an A-1 mechanism in the studied range.*

Keywords: Acid-catalyzed hydrolysis; benzoxathiazole; cyclic sulfamate; excess acidity

INTRODUCTION

The alkaline hydrolysis of a number of substituted cyclic sulfamates and their reactions with nucleophiles have been studied in detail,[1–4] but there has been no systematic investigation of the acid catalysed hydrolysis of cyclic sulfamates.

The acid catalysed hydrolysis of a number of related cyclic systems containing both sulfur (IV) and sulfur (VI) have, however, been studied by Tillett and coworkers.[5,6] The hydrolysis of the cyclic amidosulfide **2** and the sultam **3** follow an A-2 mechanism. In both cases rapid protonation on nitrogen is followed by N—S bond cleavage in the slow step.

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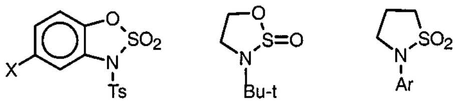


1 2 3

a: X = Me
b: X = H
c: X = Cl
d: X = NO_2

STRUCTURES 1

We now report a detailed study of the acid catalysed hydrolysis of the cyclic sulfamates **1a–d**. This class of compound is of interest for its practical use as a possible medicinal agent.[7,8]

RESULTS AND DISCUSSION

The first order rate coefficients, k_1, for the hydrolysis of **1b** in aqueous solutions of mineral acids are shown in Figure 1. In both cases the rates of hydrolysis increased continuously with increasing concentration of acids in the studied range. There is no indication of a rate maximum even at quite high acidity. The hydrolysis reaction was very slow in hydrochloric acid solutions therefore no kinetic data were obtained.

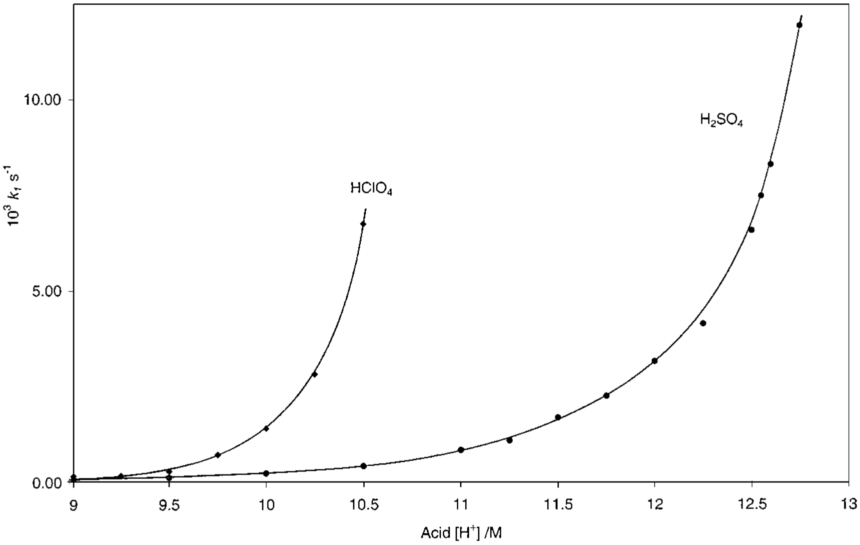


FIGURE 1 Hydrolysis of **1b** in aqueous acidic solutions at 50.0°C. ●, H_2SO_4; ◆, $HClO_4$.

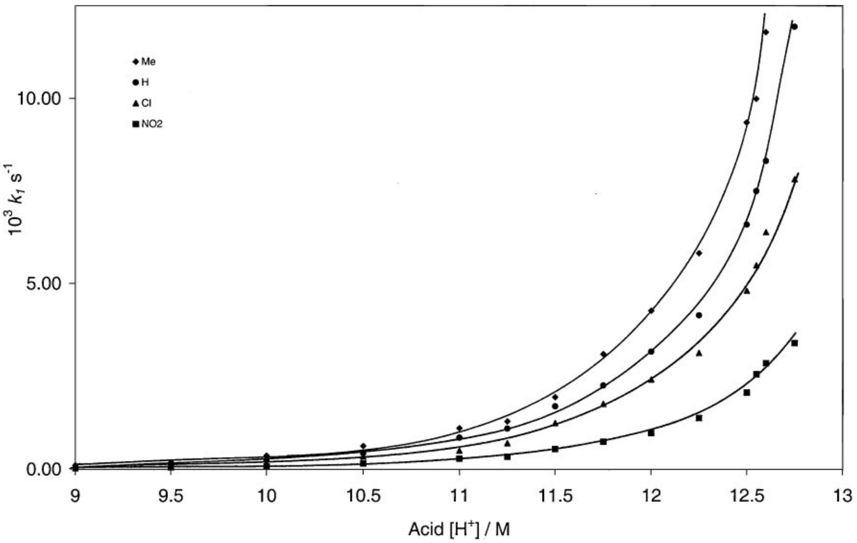


FIGURE 2 Plots of k_1 for the sulfuric acid catalysed hydrolysis of **1a–d** at 50.0°C. ♦, Me; ●, H; , Cl; ■, NO_2.

The order of catalytic effectiveness of added acids for the hydrolysis of **1b** was $HClO_4 > H_2SO_4 \gg HCl$. Bunton and his coworkers[9] have suggested that such an order ($HClO_4 > H_2SO_4 > HCl$) is characteristic of an A-1 mechanism, positive character of transition states being preferentially stabilised by anions of low charge density such as ClO_4^-, whereas the converse is the case for A-2 reactions. The acid catalysed hydrolysis profile is similar to **1a–d** in sulfuric acid solutions as shown in Figure 2.

The kinetic data in Table I were also analysed by the Excess Acidity treatment of Cox and Yates.[10,11] The appropriate kinetic equation for mainly unprotonated substrates Eq. 1 was used. Due to the low basicity of the sulfamates, the protonation correction term, $[\log C_S/(C_S + C_{SH^+})]$ can be neglected. In the equation k_1 is the pseudo first order rate constant in aqueous acid concentration $C_H{}^+$ and of excess acidity X and

$$\log k_1 - \log C_H{}^+ - \log C_S/(C_S + C_{SH^+}) = m^{\neq} m^{*} X + \log a_{Nu} + \log(k_o/K_{SH}{}^+) \tag{1}$$

$m^{\neq}\, m^{*}$ is the combined slope parameter, where $m^{\neq}$ is characteristic of the type of reaction (for A1 processes $m^{\neq} > 1$[10]), and m^{*} values give information about the protonation site. For nitrogen compounds m^{*} is in the range of 0.7 to 1.[12] Plots of $\log k_1 - \log C_H{}^+$ versus X are shown in

TABLE I Values of $10^4\ k_1\ (s^{-1})$ for the Hydrolyses of **1a–d** at 50°C

$[H^+]$ (M)	**1a** (H_2SO_4)	**1b** (H_2SO_4)	**1c** (H_2SO_4)	**1d** (H_2SO_4)	**1b** ($HClO_4$)
9.00	1.08	0.71	0.49	0.26	0.80
9.25					1.89
9.50	1.85	1.32	1.02	0.51	2.97
9.75	—	—	—	—	7.29
10.00	3.65	2.41	1.57	0.78	14.1
10.25	—	—	—	—	28.2
10.50	6.21	4.23	3.36	1.56	67.5
11.00	11.0	8.44	4.99	2.84	—
11.25	12.8	10.9	6.97	3.38	—
11.50	19.3	16.9	12.4	5.43	—
11.75	30.9	22.5	17.5	7.42	—
12.00	42.6	31.5	24.1	9.71	—
12.25	58.2	41.4	31.2	13.7	—
12.50	93.5	65.9	48.0	20.5	—
12.55	99.9	75.0	54.9	25.5	—
12.60	117	83.1	63.8	28.5	—
12.75	151	119	78.2	33.8	—

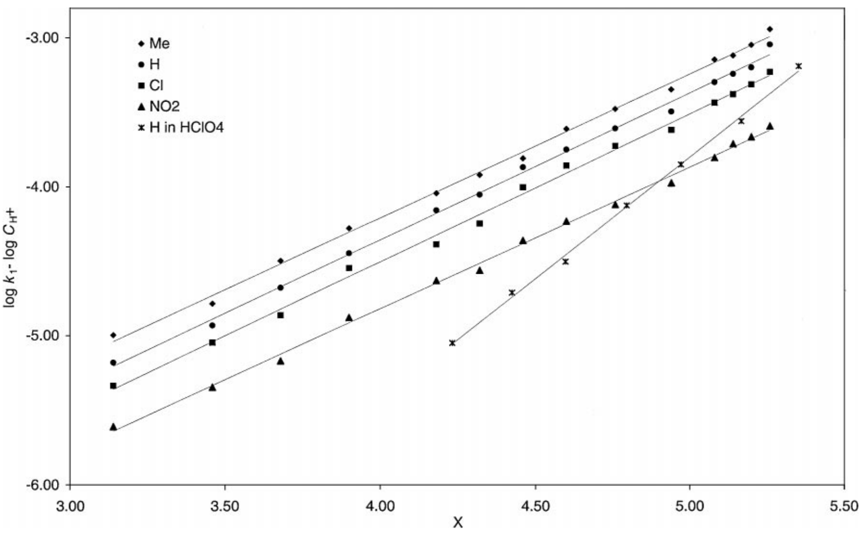


FIGURE 3 Plots of $\log k_1 - \log C_H{}^+$ vs excess acidity for the acid catalysed hydrolysis of **Ia–d** at 50.0°C. ♦, Me; ●, H; ■, Cl;   ; NO_2, ∗; **Ib** in $HClO_4$.

TABLE II Excess Acidity Treatment of the Hydrolyses of **1a–d** in Aqueous Sulfuric Acid

Compounds	Substituent	$m^{\neq}m^{*}$	$\log (k_o/K_{SH^+})$	N[b]	r^2
1a	Me	0.952	−8.63	14	0.9978
1b	H	0.996	−8.48	14	0.9965
1c	Cl	0.986	−8.30	13	0.9976
1d	NO_2	0.965	−8.07	14	0.9975
1b[a]	H	1.635	−11.98	7	0.9981

[a] In aqueous perchloric acid. [b] Number of data points.

Figure 3 for the hydrolyses of **1a–d** in sulfuric acid and for **1b** in perchloric acid.

The straight lines obtained for all compounds are characteristic of an A-1 process, which means there is no involvement of nucleophile in the transition state. The slope and intercept values for **1a–d** are given in Table II.

The temperature dependence of the rate constants of the hydrolysis reaction was analysed by a least-square procedure and calculated activation enthalpy and entropy values are shown in Table III. Acid catalysed hydrolysis of esters and amides[13] proceeding by an A-1 mechanism have $\Delta S^{\neq} \approx 0$ to 41.8 $Jmol^{-1}K^{-1}$, while those proceeding by an A-2 mechanism $\Delta S^{\neq} \approx -62.8$ to -125.5 $Jmol^{-1}K^{-1}$. Over the range 9.0–12.7 molar sulfuric acid, the values of $\Delta S^{\neq}$ for the hydrolysis of 1a–d become increasingly less negative with increase of acidity suggesting a mechanistic changeover from A-2 to A-1 (Table IV). Similar

TABLE III Values of $10^4\ k_1\ (s^{-1})$ for the Hydrolysis of the **1a–d** at Different Temperatures

Acid (M)	Compounds	60.0°C	65.0°C	70.0°C	75.0°C
9.00 H_2SO_4	**1a**	2.75	4.52	7.14	1.15
	1b	1.93	3.16	5.17	8.56
	1c	1.61	2.67	4.46	7.38
	1d	0.74	1.28	2.12	3.60
		45.0°C	50.0°C	55.0°C	60.0°C
12.75 H_2SO_4	**1a**	96.6	151	244	386
	1b	69.8	119	199	308
	1c	48.6	77.9	131	210
	1d	19.4	33.8	56.4	88.7
9.25 $HClO_4$	**1b**	1.14	1.89	3.20	5.34
10.50 $HClO_4$		38.5	67.5	115	186

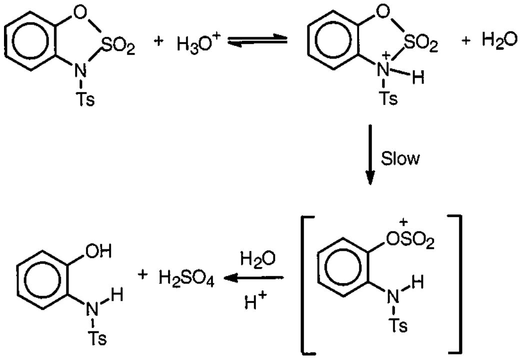
TABLE IV Arrhenius Parameters for the Hydrolysis of **1a–d** in Different Acids

Compounds	Acid	$[H^+]$/mol dm^{-3}	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})
1a	H_2SO_4	9.00	−38.41 ± 2.64	91.73 ± 0.90
1b			−29.65 ± 3.64	95.66 ± 1.24
1c			−24.33 ± 2.43	97.93 ± 0.83
1d			−22.76 ± 3.11	101.57 ± 1.06
1a	H_2SO_4	12.75	−27.81 ± 4.05	81.60 ± 1.32
1b			−11.62 ± 6.26	87.54 ± 2.04
1c			−18.04 ± 4.80	86.52 ± 1.56
1d			−15.98 ± 6.18	89.53 ± 2.01
1b	$HClO_4$	9.25	−35.44 ± 3.67	90.91 ± 1.19
		10.50	−6.56 ± 4.08	92.61 ± 1.33

behavior has been observed for the acid catalysed hydrolysis of sulfonimidic esters[14] and hydroxamic acids.[15]

The value obtained for deuterium kinetic solvent isotope effect, k_1D_2O/k_1H_2O for the hydrolysis of the **1b** in 12.65 M sulfuric acid is characteristic of a reaction that proceeds via an A-1 mechanism.[16] The value in 9.25 M sulfuric acid suggest a changeover from an A-2 mechanism even though such a mechanism seems undetectable in the acid-rate profiles (Figures 1 and 2). Similar behavior has, however, been observed in other acid-catalysed hydrolyses e.g. benzoic anhyride.[17]

In the acidity range studied, electron donating substituents produce the highest rate of hydrolysis (i.e., **1a** > **1d**) and the substituents effects are well correlated by a satisfactory Hammett $\rho\sigma$ plot [at 10.00 M H_2SO_4, $\rho = -0.81$ (corr. 0.963) and 12.75 M H_2SO_4, $\rho = -0.83$ (corr. 0.984)]. Clearly at these acidities electron-donating substituents both facilitate protonation of the substrate and stabilise the sulfur cation in the A-1 mechanism as shown in Scheme 1.



SCHEME 1

EXPERIMENTAL

Material

Sulfamates were prepared as described by Andersen and his coworkers.[2,3] Sulfamate **1a** had m.p. 166–167°C (lit[2]., 167–168°C), **1b** had m.p. 131–132°C (lit[2]., 130–131°C), **1c** had m.p. 142–143°C (lit[2]., 142–144°C) (Found: C, 43.55; H, 2.83; N, 3,76.Calc. for $C_{13}H_{10}NS_2O_5Cl$: C, 43.40; H, 2.80; N, 3.89%), **1d** had m.p. 176–178°C (lit[2]., 177–178°C).

Kinetic Procedure

The rates of hydrolysis of the sulfamates were followed at 240 nm with using a GBC Cintra 20 model spectrophotometer fitted with a thermostated cell holder (±0.05°C). Good first-order behavior was observed with clean isobestic points. Values of the first order rate coefficients k_1 were calculated from the standard equation using a least-squares procedure.

Product Analysis

The product of hydrolysis was determined by comparing the UV spectrum obtained at the completion of kinetic experiment with the spectrum of expected product, run at the same concentration and under the same conditions. The UV spectra of the product of hydrolysis were shown to be identical to that of corresponding N-tosyl-2-hydroxyanilines. Also the product of the hydrolysis of a typical sulfamate (**Ib**) isolated and recrystallised from ethanol was found to be N-tosyl-2-hydroxyaniline, m.p. 137–138°C. The structure of this compound was confirmed by ^1H and IR spectra.

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