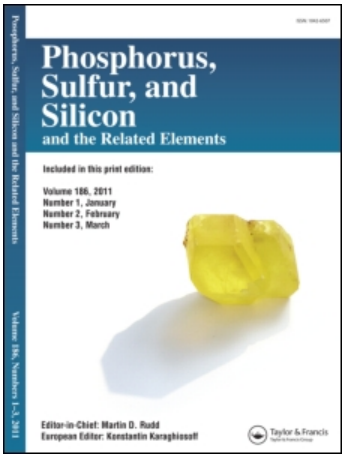

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The Synthesis and Substituent Effect of the Acid Catalyzed Hydrolysis of Amidosulfites

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*The acid-catalyzed hydrolysis of 2-oxo-3-(p-substituted)-phenyl-5-methyl-1,2,3-oxathiazolidines (**1**) have been studied in 60% (v/v) 1,4 dioxane-aqueous solutions of perchloric and hydrochloric acids at 10.0 ± 0.05°C. The analysis of the kinetic data by the order of the catalytic effects of the acids, activation parameters, kinetic solvent isotope effect, and substituent effect are all in agreement with an A-2 mechanism in the studied range.*

Keywords Acid-catalyzed hydrolysis; amidosulfites; oxathiazolidines; substituent effect

INTRODUCTION

In the literature, the first reported amidosulfite was 2-oxo-1,2,3-oxathiazolidine (**2**), which was prepared by J.A. Deyrup and C.L. Moyer by the reaction of β-amino alcohols with thionyl chloride in the presence of base in good to excellent yields.[1] The structure of (**2**) constitutes the first example of the 1,2,3-oxathiazolidine heterocyclic ring system.

In 1976, the 2-oxo-1,2,3-oxathiazolidines (**2**), were reported effectively to inhibit the growth of *Staphylococcus aureus* and *Escherichia coli*.[2]

The first kinetic study of the acid-catalyzed ring opening of this class of compound on 3-tert-butyl-1,2,3-oxathiazolidine-2-oxide with up to 2.0 M aqueous mineral acids was studied by Cox and his colleagues by using a stopped-flow spectrophotometer, and they suggested an A-2 mechanism in this range.[3] The kinetics and mechanism of the hydrolysis of 2-oxo-3-(p-substituted)-phenyl-5-methyl-1,2,3-oxathiazolidine

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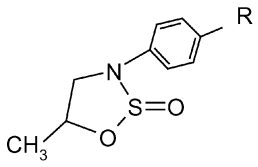
(**1a–c**) have been studied in 60% (v/v) 1,4-dioxane-aqueous solutions of perchloric and hydrochloric acids at $10.0 \pm 0.05^{\circ}C$.

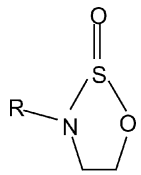
There has been no systematic study of the acid-catalyzed hydrolysis of 1,2,3-oxathiazolidines in acidic solutions. We now report a complementary study of the acid-catalyzed hydrolysis of a series of 2-oxo-3-(p-substituted)-phenyl-5-methyl-1,2,3-oxathiazolidines (**1a–c**) in 60% (v/v) 1,4-dioxane-aqueous solutions of mineral acids.

RESULTS AND DISCUSSION

The first-order rate coefficients, k_1, for the hydrolysis of 2-oxo-3-(p-methyl)-phenyl-5-methyl-1,2,3-oxathiazolidine (**1a**) in aqueous 60% (v/v) dioxane solutions of mineral acids are shown in Figure 1, Scheme 1.



1 **a**, R = CH_3
b, R = H
c, R = Cl



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SCHEME 1

In all cases, the rate of hydrolysis increases continuously with increasing acid concentration (Table I). Due to the high reactivity of the oxathiazolidines, the hydrolysis proceeds very rapidly; therefore, it cannot be followed in sulfuric acid by a UV spectrometer at $10.0 \pm 0.05^{\circ}C$. It also was difficult to follow the reaction above 0.6 M HCl and $HClO_4$ at this temperature. The order of catalytic effectiveness of the added acids observed for the hydrolysis of the amidosulfite was $H_2SO_4 > HCl > HClO_4$. Bunton and colleagues[4] suggested that such an order is characteristic of a bimolecular (A-2) mechanism, in which a developing positive character in transition states being preferentially stabilized by anions of high charge density such as Cl^-, whereas the converse, is usually the case for an unimolecular (A-1) mechanism ($HClO_4 > HCl > H_2SO_4$).

The temperature dependence of the rate constants of the hydrolysis reaction was studied at different temperatures and analyzed by a least-squares procedure using a computer program (Eyring equation). Entropies of activation ($\Delta S^{\neq}$) have been used as mechanistic criteria for distinguishing between A-1 and A-2 mechanism;[5,6] generally, an

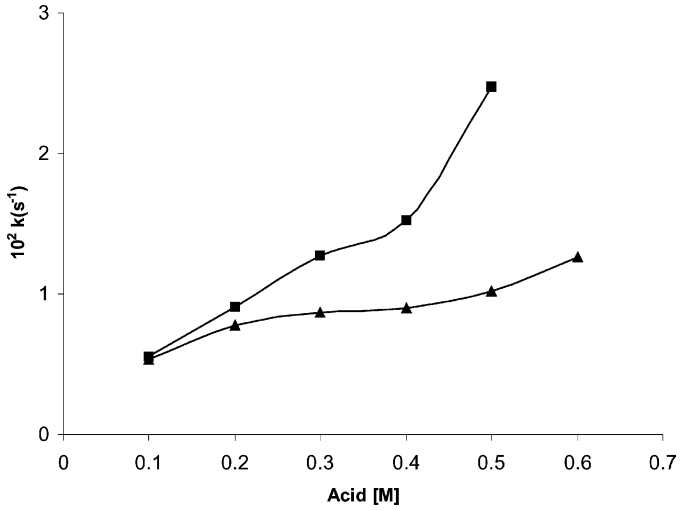


FIGURE 1 The acid-catalyzed hydrolyses of 2-oxo-3-(p-methyl)-phenyl-5-methyl-1,2,3-oxathiazolidines in the presence of 60% dioxane-water (v/v) at $10.0 \pm 0.05^{\circ}$C. (■, HCl; ▲, $HClO_4$)

A-1 mechanism is expected to have a more positive value than the corresponding an A-2 mechanism.

The calculated entropies of activation as shown in Table II also support suggested an A-2 reaction mechanism of the hydrolysis should be reaction mechanism for the hydrolysis of the amidosulfites. Values of the entropy of activation for the hydrolysis of the (**1a**) ($\Delta S^{\neq} = -93.69, -94.23$ JK^{-1} mol^{-1}) for 0.10 M perchloric and 0.10 M hydrochloric acids, respectively. It is suggested that the

TABLE I Values of 10^2 k_1 (s^{-1}) for the Hydrolyses of 2-Oxo-3-(p-substituted)-phenyl-5-methyl-1,2,3-oxathiazolidines in the Presence of 60% Dioxane-Water (v/v) at $10.0 \pm 0.05^{\circ}$C

$[H^+](M)$	**1a** ($HClO_4$)	**1a** (HCl)	**1b** ($HClO_4$)	**1b** (HCl)	**1c** ($HClO_4$)	**1c** (HCl)
0.10	0.54	0.56	2.58	1.85	1620	2503
0.20	0.78	0.91	5.66	4.30	2900	3635
0.30	0.87	1.27	10.1	7.53	3980	4287
0.40	0.90	1.53	14.7	10.7	–	–
0.50	1.02	2.47	20.7	15.9	–	–
0.60	1.26	–	29.8	24.8	–	–

TABLE II Arrhenius Parameters for the Hydrolysis of 2-Oxo-3-(p-substituted)-phenyl-5-methyl-1,2,3-oxathiazolidines in the Presence of 60% Dioxane-Water (v/v) at 10.0 ± 0.05°C

Compound	Acid	$[H^+]$/M	$\Delta H^{\neq}$ (kJmol^{-1})	$\Delta S^{\neq}$ (JK^{-1} mol^{-1})	R^2
1a	$HClO_4$	0.10	55.29	−93.69	0.997
	HCl	0.10	55.06	−94.23	0.998
1b	$HClO_4$	0.10	51.94	−92.43	0.992
		0.30	48.98	−91.78	0.996
	HCl	0.10	55.05	−84.09	0.995
		0.30	56.47	−67.55	0.999

negative values of $\Delta S^{\neq}$ for an A-2 mechanism is a reflection of the loss of rotational and translational freedom of water molecules in the transition state, where a water molecule acts as a nucleophile. The acid-catalyzed hydrolysis of esters and amides[6] proceeding by an A-1 mechanism have $\Delta S^{\neq} \approx 0$ to -41.8 JK^{-1} mol^{-1}, while those proceeding by an A-2 mechanism have $\Delta S^{\neq} \approx -62.8$ to -125.5 JK^{-1} mol^{-1}.

The value obtained for the deuterium Kinetic Solvent Isotope Effect (KSIE) ($k_1^{D_2O}/k_1^{H_2O}$) for the sulfuric acid-catalyzed hydrolysis of 2-oxo-3-phenyl-5-methyl-1,2,3-oxathiazolidine is 1.12 (Table III). The values of KSIE for the hydrolysis of amidosulfites are comparable to those of 3-chloropropyl-p-toluenesulfinate[7] ($k^{D_2O}/k^{H_2O} = 1.78$ in 1.0 M HCl) and p-nitrophenyl-N-aroyl-p-tolueneiminosulfonate[8] ($k^{D_2O}/k^{H_2O} = 1.63$ in 3.0 M $HClO_4$) and N-(4-substituted-arylsulfinyl)phthalimides[9] ($k^{D_2O}/k^{H_2O} = 1.02$ in 1.0 M H_2SO_4), which hydrolyze by a normal A-2 mechanism.

TABLE III Deuterium Solvent Isotope Effect for the Hydrolysis of 2-Oxo-3-phenyl-5-methyl-1,2,3-oxathiazolidine in 60% Dioxane-Water (v/v)

Temperature (°C)	Acid solutions	$10^2\ k_1$(s^{-1})	$10^2\ k_1$ average (s^{-1})	$k_1^{D2O}/k_1^{H_2O}$
10.0 ± 0.05	0.1 M H_2SO_4	2.47		
		2.47	2.47	
		2.46		1.12
10.0 ± 0.05	0.1 M D_2SO_4	2.78	2.77	
		2.76		

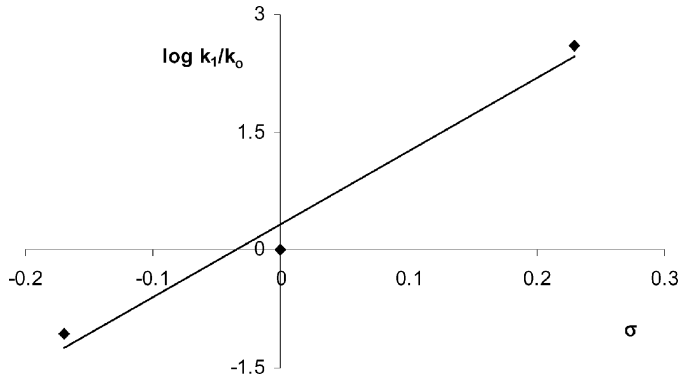


FIGURE 2 The plot of log k_1 versus Hammett σ values for the acid-catalyzed hydrolyses (0.30 M $HClO_4$) of 2-oxo-3-(p-substituted)-phenyl-5-methyl-1,2,3-oxathiazolidines in the presence of 60% dioxane-water (v/v) at $10.0 \pm 0.05^{\circ}$C.

In the studied acidity range, electron-withdrawing substituents produce the highest rate of hydrolysis, and the substituent effects are well correlated by a satisfactory Hammett plot [at 0.30 M $HClO_4$, $\rho = 9.27$ (corr. 0.978) and 0.30 M HCl, $\rho = 3.79$ (corr. 1.00)] as shown in Figures 2 and 3 respectively. Clearly at these acidities, an electron-withdrawing substituent increases the positive charge on a sulfur atom, and water can attack rapidly to the sulfur atom in the rate-limiting step for an A-2 mechanism. There is no direct evidence concerning the site of the protonation of amidosulfites; however, the protonation of sulfinamides[10,11] and sultams[12] occur preferentially at the nitrogen atom.

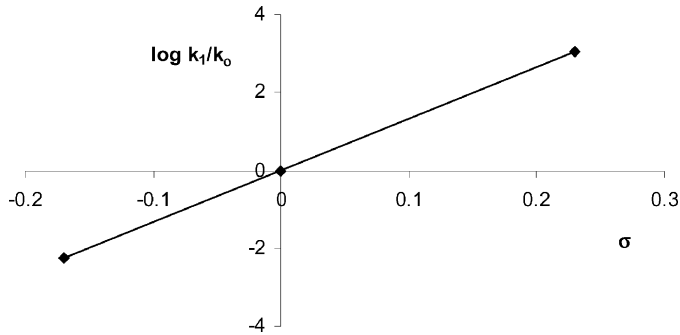
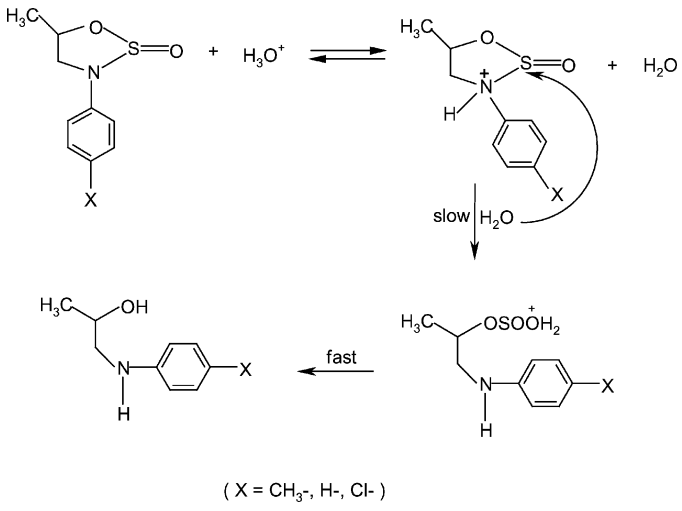


FIGURE 3 The plot of log k_1 versus Hammett σ values for the acid-catalyzed hydrolyses (0.30 M HCl) of 2-oxo-3-(p-substituted)-phenyl-5-methyl-1,2,3-oxathiazolidines in the presence of 60% dioxane-water (v/v) at $10.0 \pm 0.05^{\circ}$C.



SCHEME 2

In the light of the overall evidence, we propose that the acid-catalyzed hydrolysis of 2-oxo-3-(p-substituted)-phenyl-5-methyl-1,2,3-oxathiazolidines in 60% (v/v) 1,4-dioxane-aqueous solutions occurs by the an A-2 mechanism, as shown in Scheme 2. In this first step, a rapid preequilibrium protonation of 2-oxo-3-(p-substituted)-phenyl-f-methyl-1,2,3-oxathiazolidine takes place. It is assumed that the protonation occurs on nitrogen atom and a water molecule attacks to sulfur atom as nucleophile in the rate determining step.

EXPERIMENTAL

Materials

2-oxo-3-(p-substituted)-phenyl-5-methyl-1,2,3-oxathiazolidines (**1a–c**) were prepared from the corresponding N-sulfinyl-p-substituted anilines with propylene oxide in the presence of LiCl in DMF as described by Nishiyama and Yamada.[13] This involved the reaction of thionyl chloride with (p-substituted)-aniline in benzene to give the N-sulfinyl-p-substituted anilins.[14] **1a**, had m.p. 85°C (lit[13]., 83.2–85°C); ^{1}H NMR (acetone-d_6), δ 1.16–1.63 (dd, 3H), 2.27 (s, 3H), 3.66 (t, 1H), 3.93 (q, 1H), 4.98 (m,1H), 6.59–7.14 (m,4H); **1b**, had m.p. 58°C (lit[13]., 59.3–59.8°C); ^{1}H NMR (acetone-d_6), δ1.58 (d, 3H), 3.40 (t, 1H), 4.02 (q, 1H), 5.43 (m, 1H), 6.58–7.37 (m, 5H); **1c**, m.p. 92°C (lit[13]., 91.8–92.6°C).

Kinetic Procedure

The rates of the acid-catalyzed hydrolysis of 2-oxo-3-(p-substituted)-phenyl-5-methyl-1,2,3-oxathiazolidines were followed spectrometrically at 190–400 nm using a GBC Cintra 20 Model UV-VIS spectrophotometer with a thermostatted cell compartment ($10 \pm 0.05^{\circ}$C). Values of k_1 were calculated from the standard equation using a least-squares procedure. All kinetic measurements were duplicated, and the average deviation from the mean was $<5\%$.

Product Analysis

The product of the hydrolysis was determined by comparing the UV spectrum obtained at the completion of the kinetic experiment with the spectrum of the expected product which was run at the same concentration and under the same conditions. The UV spectra of the hydrolysis of 2-oxo-3-(p-chloro)-phenyl-5-methyl-1,2,3-oxathiazolidine (**1c**) were shown to be identical to that of the corresponding 1-(4-cholorophenylamino)-propane-2-ol, which was prepared from 4-chloroaniline with propylene oxide in ethanol. 1-(4-chlorophenylamino)-propane-2-ol, m.p. 40–41°C; (Found: C, 58.63; H, 6.74; N, 7.49. Calc. for $C_9H_{12}NOCl$: C, 58.22; H, 6.53; N, 7.55%).

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