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ACID-CATALYSED HYDROLYSIS OF S(IV)N BOND IN N-SULPHONYL SULPHILIMINES—I

MECHANISM AND SUBSTITUENT EFFECT

I. KAPOVITS, F. RUFF and Á. KUCSMAN
Institute of Organic Chemistry, L. Eötvös University, Budapest, Hungary

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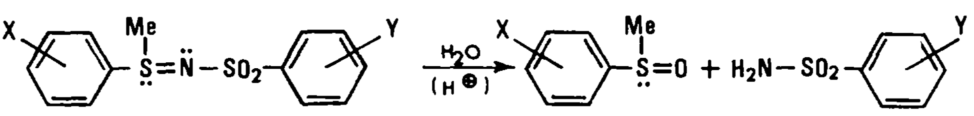
Abstract—The acid-catalysed hydrolysis of sulphilimines of $XC_6H_4(Me)SNTs$ and $MePhSNSO_2C_6H_4Y$ type has been studied by a kinetic method in moderately concentrated (1–6 M) aqueous H_2SO_4 and $HClO_4$ solutions. The rate law: rate = k_ψ[sulphilimine] is valid for hydrolysis leading to sulphoxides and sulphonamides. The dependence of k_ψ on acidity, temperature and substituents X and Y has been measured and interpreted. ρ_X, ρ_Y and $\Delta S^‡$ data ($+1{\cdot}19$, $+1{\cdot}00$ and $-18{\cdot}7$– – $22{\cdot}6$ e.u., resp) show that the nucleophilic attack of water on the positively polarized S(IV) atom of protonated sulphilimines can be regarded as the rate-determining step of the hydrolysis. From ϕ parameters (0·94–1·5) calculated for the hydrolysis of MePhSNTs it follows that water participates in the reaction as a nucleophile and proton-transfer agent.

INTRODUCTION

RECENTLY attention has been focused on the investigation of the reactivity of the SN bond in organic compounds; in most cases N-sulphonyl sulphilimines containing SN bonds of intermediate bond order[1] ($R^1R^2S{\cdots}\ddot{N}{-}SO_2R^3$) were used as model compounds.[2] N-Sulphonyl sulphilimines can be hydrolysed to sulphoxides (R^1R^2SO) and sulphonamides ($R^3SO_2NH_2$),[3] but only the alkaline hydrolysis has been examined thoroughly.[2]

In order to elucidate the mechanism of the acid-catalysed sulphilimine hydrolysis, we investigated the reaction of some sulphilimines of type I in moderately concentrated (1–6 M) aqueous sulphuric and perchloric acid solutions. As shown, reaction (1) proceeds quantitatively and can be followed by kinetics.



I II III

Y = *p*-Me; X = *p*-OMe, H, *m*-OMe, *p*-Cl, *m*-Cl
X = H; Y = *p*-OMe, *p*-Me, H, *p*-Cl (1)

In an accompanying paper[4] it has been reported that sulphilimines of type I are moderately strong Hammett-bases with pK_a's between $-1{\cdot}8$ and $-3{\cdot}0$. Consequently, sulphilimines, when dissolved in aqueous mineral acids, are to a significant extent transformed into their protonated forms in a rapid equilibrium reaction. Therefore the nucleophilic attack of water on the positively polarized S (IV) atom of N-protonated sulphilimines is probably the rate-determining step of the hydrolysis.

$$R^1R^2\ddot{S}{=}\dot{N}SO_2R^3 + H^{\oplus} \rightleftharpoons [R^1R^2\ddot{S}{=}\overset{\oplus}{\dot{N}}HSO_2R^3 \leftrightarrow R^1R^2\overset{\oplus}{\underset{..}{S}}{-}\dot{N}HSO_2R^3] \xrightarrow{H_2O} \text{Hydrolysis products} \qquad (2)$$

Scheme (2) which is similar to that of acid-catalysed hydrolysis of carboxamides involves the pseudo-unimolecular rate-law: rate = $k_\psi[S]_{st}$ where k_ψ and $[S]_{st}$ represents the rate constant and the stoichiometric concentration of the sulphilimine substrate, resp. If this is true for sulphilimine hydrolysis, then the dependence of k_ψ on acidity, temperature and substrates will indicate the manner in which water participates in the rate-determining step, and how the stability of the transition state is influenced by substituents X and Y.

RESULTS AND DISCUSSION

Determination of rate constant k_ψ *for the hydrolysis of* MePhSNTs

As shown by kinetic measurements, the hydrolysis of MePhSNTs in moderately concentrated (1–6 M) aqueous sulphuric and perchloric acid solutions proceeds according to the rate law: rate = $k_\psi[S]_{st}$. The k_ψ's determined in solutions of different acidity are listed in Tables 1 and 2. These data indicate that k_ψ values go through a maximum as the concentration of acid is increased. A similar phenomenon has been observed in studies on acid-catalysed hydrolysis of carboxamides.[5] The concentrations of sulphuric and perchloric acids for maximum rate of sulphilimine hydrolysis are 3·4 M and 3·3 M, resp. The plotting of log k_ψ *vs* $-H_0$ also gives a typical maximum curve. Edward *et al.*[5] have suggested that such a rate profile is due to the considerable decrease of water activity in concentrated acid solutions.

TABLE 1. RATE COEFFICIENTS FOR THE HYDROLYSIS OF MePhSNTs IN H_2SO_4 SOLUTION AT 50°

H_2SO_4				
[M]	$H_0{}^a$	$10^5 \cdot k_\psi$ (sec^{-1})	$10^5 \cdot k_2$ ($l.mol^{-1} \cdot sec^{-1}$)	$10^4 \cdot k_p$ (sec^{-1})
0·99	−0·26	2·05	1·04	19·35
1·48	−0·55	3·09	1·07	15·10
2·01	−0·85	4·46	1·16	11·15
2·63	−1·19	5·66	1·17	6·78
2·93	−1·34	6·10	1·18	5·35
2·98	−1·37	6·36	1·21	5·24
3·42	−1·58	6·61	1·18	3·62
3·48	−1·60	6·52	1·16	3·44
3·87	−1·79	6·85	1·20	2·57
4·49	−2·06	5·65	1·05	1·40
5·04	−2·30	4·49	0·96	0·83
5·40	−2·46	3·48	0·87	0·55
6·03	−2·78	1·46	0·55	0·19

[a] Values of H_0 are taken from Long and Paul's review[9].

Calculation of rate constant k_2 *for the hydrolysis of* MePhSNTs

Since the hydrolysis of sulphilimines and that of carboxamides investigated by

TABLE 2. RATE COEFFICIENTS FOR THE HYDROLYSIS OF MePhSNTs IN $HClO_4$ SOLUTION AT 50°

$HClO_4$				
[M]	H_0*	$10^5 \cdot k_\psi$ (sec^{-1})	$10^5 \cdot k_2$ (l.mol^{-1}·sec^{-1})	$10^4 \cdot k_p$ (sec^{-1})
1·00	−0·22	1·55	1·57	16·03
1·50	−0·53	2·31	1·57	12·17
2·00	−0·78	2·89	1·50	8·43
2·41	−0·97	3·36	1·47	6·46
2·92	−1·19	3·69	1·38	4·42
3·27	−1·36	3·73	1·30	3·14
3·52	−1·49	3·72	1·25	2·42
3·88	−1·66	3·49	1·14	1·65
4·53	−1·99	2·90	1·01	0·80
5·18	−2·33	1·84	0·80	0·33
5·37	−2·45	1·46	0·72	0·24
5·79	−2·71	0·86	0·60	0·12

* Values of H_0 are taken from Long and Paul's review[9]

Edward *et al.*[5] show an analogous rate profile, the former reaction may be similarly interpreted. In the case of sulphilimines, scheme (3) is to be considered where the reaction of water with N-protonated sulphilimine is rate-controlling.

$$S + H_3O^{\oplus} \underset{K_a}{\rightleftharpoons} SH^{\oplus} + H_2O \overset{K_2}{\rightleftharpoons} \text{Transition state} \xrightarrow{k} \rightarrow \text{Hydrolysis products} \tag{3}$$

Assuming that it is only the equilibrium concentration of a protonated sulphilimine as key-intermediate that changes with the increase of the concentration of acid in diluted solutions, we obtain the rate law: rate $= k_2[S][H_3O^+]$. The "second order rate constant" k_2 can be correlated to k_ψ according to Eq. (4).*

$$k_\psi = k_2 K_a [H_3O^+]/(K_a + h_0) \tag{4}$$

As expected, k_2 is nearly constant in the region of low acidity (Tables 1 and 2). Thus, Eq. (4) gives a satisfactory theoretical rate-acidity profile up to the maximum of k_ψ.

Calculation of rate constant k_p *for the hydrolysis of* MePhSNTs

As pointed out, the reaction of protonated sulphilimines with water can be regarded as the rate-determining step of sulphilimine hydrolysis. Since the reaction media used contained water in a great excess, it was necessary to define and calculate a first-order rate constant k_p based on the concentration of the protonated sulphilimine only (rate $= k_p[SH^+]$). N-sulphonyl sulphilimines behave as Hammett-bases,[4] therefore k_p is related to the empirical first-order rate constant k_ψ (based upon the stoichiometric concentration $[S]_{st}$ of sulphilimine) according to Eq. (5).†

$$k_p = k_\psi \frac{[S]_{st}}{[SH^+]} = k_\psi \frac{[S] + [SH^+]}{[SH^+]} = k_\psi \frac{h_0 + K_a}{h_0} \tag{5}$$

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* k_ψ, $[H_3O^+]$, H_0 and K_a values are given in Tables 1, 2 and 4.

† k_ψ, H_0 and K_a data are listed in Tables 1, 2 and 4.

The importance of medium effect is well reflected in the dependence of k_p on the acidity of the reaction media (Tables 1 and 2). Taking into consideration the changes of k_p under different conditions, one can investigate the role of water in the hydrolysis reaction (see below), and compare the relative reactivities of protonated sulphilimines with different S-aryl and N-acyl substituents (see later).

The role of water in the rate-determining step of the hydrolysis of MePhSNTs

In order to characterise the kinetic effect of changing the reaction medium for the hydrolysis reaction of MePhSNTs, the Bunnett–Olsen's[6] slope-parameter ϕ has been

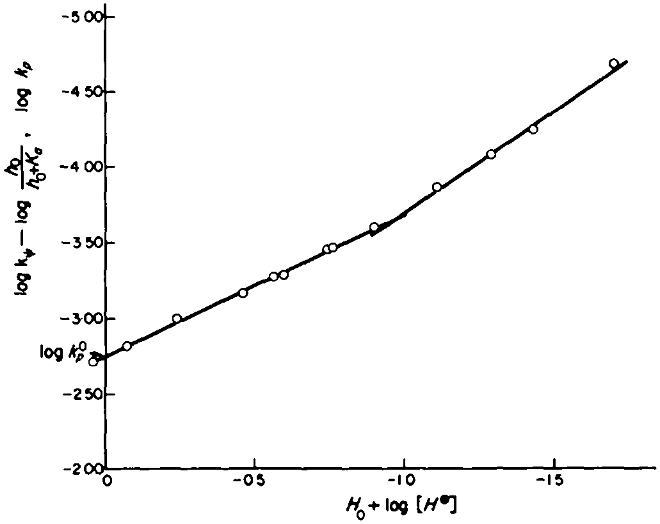


FIG. 1. Correlation of [log k_ψ − log $h_0/(h_0 + K_a)$] for MePhSNTs hydrolysis in H_2SO_4 solution with (H_0 + log [H^+])

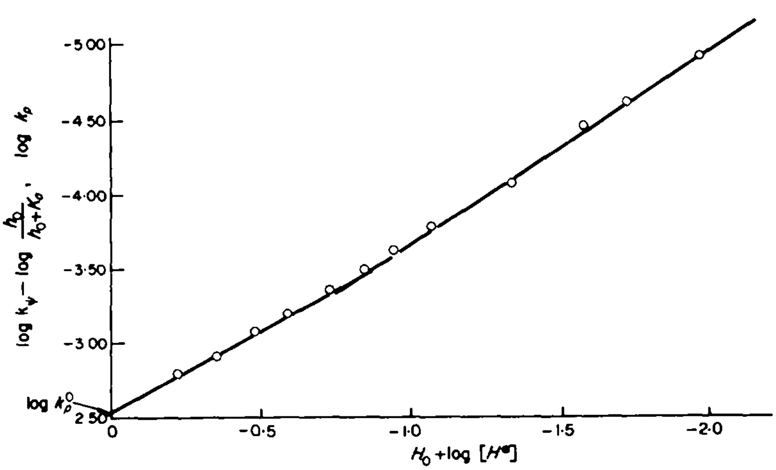


FIG. 2. Correlation of [log k_ψ − log $h_0/(h_0 + K_a)$] for MePhSNTs hydrolysis in $HClO_4$ solution with (H_0 + log [H^+])

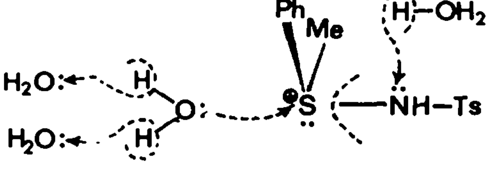
evaluated by plotting $\log k_\psi - \log h_0/(h_0 + K_a)$ (i.e. $\log k_p$: cf. Tables 1 and 2) *vs* $H_0 + \log [H^+]$. Figs 1 and 2 referring to sulphuric and perchloric acid solutions, resp. show that the plotes are not quite linear rendering the determination of ϕ values in both cases somewhat uncertain (ϕ = 1·12 and 1·25 resp.; *cf* Table 3). Nevertheless, the plots can be divided into two linear parts with somewhat different ϕ_1 and ϕ_2 slope-parameters (in sulphuric acid ϕ_1 = 0·94, ϕ_2 = 1·48: in perchloric acid ϕ_1 = 1·12, ϕ_2 = 1·30: *cf* Table 3). The point of intersection of the two straight lines corresponds to the medium where k_ψ shows a maximum. The intercepts of the linear plots for the sulphuric and perchloric acid solutions of lower acidity represent $\log k_p^0$ values for reactions at infinite dilution in water: $\log k_p^0$ = − 2·74 and − 2·54 (from Figs 1 and 2, resp.).

TABLE 3. ϕ AND w PARAMETERS FOR THE ACID-CATALYSED HYDROLYSIS OF MePhSNTs in H_2SO_4 AND $HClO_4$ SOLUTIONS AT 50°

		H_2SO_4		$HClO_4$	
		value of parameter	concentration range [M]	value of parameter	concentration range [M]
ϕ		1·12	0·99–6·03	1·25	1·00–5·79
	r[a]	±0·992		±0·998	
ϕ_1		0·94	0·99–3·87	1·12	1·00–2·92
	r[a]	±0·999		±0·999	
ϕ_2		1·48	3·87–6·03	1·30	3·27–5·79
	r[a]	±0·996		±1·000	
w		5·84	2·93–6·03	6·60	3·52–5·79
	r[a]	±0·998		±0·999	

[a] Correlation coefficient.

If the Bunnett–Olsen's classification for hydrolysis reaction is taken into account, the relatively high ϕ_1 and ϕ_2 values for sulphilimine hydrolysis (ϕ_1, ϕ_2 > 0·58) suggest that the hydration of the transition state is exceptionally high and water participates in the rate-determining step not only as a nucleophile (*cf* Equation 3), but as a proton-transfer agent, too. Indeed, it stands to reason that water as a proton-acceptor aids the nucleophilic attack of another water molecule on the S atom (to form a sulphinyl group). On the other hand, $H_3O^\oplus$ as proton-donor enhances the departure of the leaving group in the form of $TsNH_2$. The role of water in sulphilimine hydrolysis is demonstrated in scheme IV.



IV

One may arrive at a similar conclusion by plotting log k_ψ − log $h_0/(h_0 + K_a)$ (i.e. log k_p: cf. Tables 1 and 2) *vs* − log a_{H_2O}* and evaluating slope-parameter w defined in an earlier work of Bunnett.[7] The w values determined for the hydrolysis of MePhSNTs in sulphuric and perchloric acid solutions ($w = 5{\cdot}84$ and $6{\cdot}60$, resp.) are in the region $w > 3$ (*cf* Table 3).† Thus the hydrolysis of sulphilimine in moderately concentrated aqueous acids belongs to the 3rd type of reactions as classified by Bunnett. (Water acts as a proton transfer agent and the hydration of the transition state is exceptionally high.)

Determination of rate constants k_ψ *and* k_p *for the hydrolysis of* $XC_6H_4(Me)SNTs$ *and* $MePhSNSO_2C_6H_4Y$ *sulphilimines*

The substituent effect of X and Y groups. The hydrolysis of the above sulphilimines in moderately concentrated mineral acids proceeds similarly to that of MePhSNTs.

TABLE 4. RATE COEFFICIENTS AND ACTIVATION PARAMETERS FOR THE ACID-CATALYSED HYDROLYSIS OF $XC_6H_4(Me)SNTs$ SULPHILIMINES IN 2·00 M $HClO_4$ SOLUTION

X	σ_X[a]	K_a[b]	Temp. (°C)	$10^5 \cdot k_\psi$ (sec^{-1})	$10^5 \cdot k_2$ (l. mol.$^{-1}$ sec^{-1})	$10^4 \cdot k_p$ (sec^{-1})	$\Delta H^\ddagger$ (kcal· mol^{-1})	$\Delta S^\ddagger$ (e.u.)
p-OMe	−0·268	64·6	50	1·99	1·09	2·33	18·6	−22·6
			70	11·38	6·22	13·33		
H	0	170	50	2·89	1·50	8·44	19·5	−19·0
			55	4·36	2·25	12·73		
			60	7·32	3·78	21·37		
			65	11·59	5·99	33·83		
			70	17·38	8·98	50·74		
m-OMe	+0·115	182	50	2·99	1·54	9·32	19·2	−20·1
			70	17·98	9·29	56·06		
p-Cl	+0·227	245	50	3·49	1·78	14·53	19·2	−19·7
			70	21·01	10·76	87·46		
m-Cl	+0·373	302	50	3·43	1·75	17·52	19·4	−19·0
			70	21·11	10·77	107·82		

[a] The values of σ_X are taken from McDaniel and Brown's compilation[10]

[b] K_a values published in the accompanying paper[4]

The k_ψ rate constants determined for different sulphilimines in 2M perchloric acid solutions are listed in Tables 4 and 5. Since the relative reactivities of adequate N-protonated sulphilimines in aqueous acids can be compared on the basis of their k_p rate constants, these data calculated from k_ψ's by the use of Eq (5) are also given.

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* a_{H_2O} values given by Bunnett[7] were used.

† It may be mentioned here that the actual plots are fairly straight through the ranges of about 3–6 M H_2SO_4 and 3·5–5·8 $HClO_4$ concentrations, though curved on the left side (i.e. up to the acid concentration where a maximum is found for k_ψ). The w values were calculated from the straight part of the plots. Since the plots of log k_ψ − log $[HX]/(h_0 + K_a)$ are curved through the whole ranges of acid concentrations used, the w^* parameters cannot be evaluated for sulphilimine hydrolysis.

From k_p and σ_X data (Table 4) the reaction constant ρ_X for the acid-catalysed hydrolysis of $XC_6H_4S(Me)NTs$ sulphilimines has been calculated by a least-square procedure. The value obtained $\rho_X = 1{\cdot}19$ ($r = 0{\cdot}986$) indicates that hydrolysis is promoted by electron-withdrawing X groups. This is consistent with a rate-determining nucleophilic attack of water on the positively polarized S(IV) atom of the $[XC_6H_4(Me)\underset{..}{S}{=}\overset{\oplus}{N}HTs \leftrightarrow XC_6H_4(Me)\overset{\oplus}{\underset{..}{S}}{-}\ddot{N}HTs]$ substrate.

Table 5. Rate coefficients and activation parameters for the acid-catalysed hydrolysis of $MePhSNSO_2C_6H_4Y$ sulphilimines in 2·00 M $HClO_4$ solution

Y	σ_Y[a]	K_a[b]	Temp. (°C)	$10^5 \cdot k_\psi$ (sec^{-1})	$10^5 \cdot k_2$ (l. $mol.^{-1}$ sec^{-1})	$10^4 \cdot k_p$ (sec^{-1})	$\Delta H^\ddagger$ (kcal. mol^{-1})	$\Delta S^\ddagger$ (e.u.)
p-OMe	−0·268	135	50	2·70	1·41	6·32	19·4	−19·4
			70	16·64	8·69	38·90		
p-CH_3[c]	−0·170	170	50	2·89	1·50	8·44	19·5	−19·0
			70	17·38	8·98	50·74		
H	0	229	50	3·09	1·59	12·04	19·6	−18·7
			70	19·28	9·89	75·13		
p-Cl	+0·227	355	50	3·39	1·72	20·30	19·3	−19·5
			70	20·55	10·45	123·03		

[a] The values of σ_Y are taken from McDaniel and Brown's compilation[10]

[b] K_a values published in the accompanying paper[4]

[b] *cf* X=H in Table 4.

From k_p and σ_Y data (Table 5) the reaction constant ρ_Y for the acid-catalysed hydrolysis of $MePhSNSO_2C_6H_4Y$ sulphilimines can also be evaluated. $\rho_Y = 1{\cdot}00$ ($r = 0{\cdot}995$) shows that hydrolysis is promoted by electron-withdrawing Y groups too. From this fact it follows that the substituent effect of Y group is transmitted by the $—SO_2—NH—$ group. The increased reactivity of sulphilimines with an electron-withdrawing Y group may also be explained if we consider that $YC_6H_4SO_2NH_2$ seems to be a better leaving group than $C_6H_5SO_2NH_2$.

Calculation of activation parameters for the hydrolysis of $XC_6H_4(Me)SNTs$ *and* $MePhSNSO_2C_6H_4Y$ *sulphilimines*

The activation parameters $\Delta H^\ddagger$ and $\Delta S^\ddagger$ calculated from the equation $k_\psi = (kT/h) \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT)$ are given in Tables 4 and 5; k_ψ's have been measured for reactions carried out in 2M perchloric acid at 50° and 70°. $\Delta S^\ddagger$ values ($-18{\cdot}7$— $-22{\cdot}6$ e.u.) are in the range normally associated with a bimolecular mechanism and provide further support for the interpretation of sulphilimine hydrolysis as outlined above.

EXPERIMENTAL

Materials. The purity of mineral acids, sulphilimines and sulphoxides used in the kinetic measurements were checked by analysis and/or spectroscopic methods. The preparation of sulphilimines listed in Tables 4 and 5 has been published.[4]

Kinetics. The hydrolysis reactions of sulphilimines were carried out in 1–6 M aqueous H_2SO_4 and $HClO_4$ at 50° and 70° (± 0·1°). The initial concentration of sulphilimines was 10^{-3} mol/l. To diminish the concentration of the acid to 0·1 M, the samples taken from the mixtures were poured into a soln of NaOH prepared with a 1:1 (v/v) EtOH-water as solvent. The concentrations of sulphilimines and sulphoxides in the samples were measured by the polarographic method. As shown previously,[8] both sulphilimines and sulphoxides can be reduced on dropping mercury electrode: their diffusion-controlled waves are proportional to the concentrations. The half-wave potentials of sulphilimines are at about − 0·4 V, whereas those of sulphoxides in solns of pH 1 are at about − 0·9 V. The selective determination of these compounds was based on these findings. In the polarographic measurements AgCl as reference electrode was used; the solns contained 0·1 mol/l of NaCl to keep the electrode potential constant. Concentration-time plots showed that the sulphilimine consumed in the reaction was always equimolar with the sulphoxide produced. Thus, the possibility of the accumulation of an intermediate and that of a parallel reaction could be excluded. The k_ψ rate constants were calculated from the concentration-time plots using the equation $k_\psi = (1/t)\cdot 2\cdot 303\cdot \log[S]_0/[S]$. The measurements were accurate to within ± 3%.

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