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ACID-CATALYSED HYDROLYSIS OF N-SULPHONYL SULPHILIMINES—II

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Abstract—The basicity and the acid-catalysed hydrolysis of Ph(R)SNTs and *o*-XC_6H_4(Me)SNTs sulphilimines have been studied by UV spectrophotometric and kinetic methods, respectively, in aqueous $HClO_4$ (1–10 M) and 1:1 (v/v) EtOH/H_2O–$HClO_4$ (0.5–6 M). Depending on the constitution of the substrates, sulphilimine hydrolysis can follow three different courses, according to rate-acidity profiles, Bunnett–Olsen's treatment, activation parameters and product analysis. Most typical for sulphilimines is S_N2 hydrolysis with S^{IV}–N bond cleavage. In this case the reaction starts with the nucleophilic addition of water and is promoted by acid-base catalysis. If a relatively stable carbenium ion can be formed from R group, an S_N1 reaction with S^{IV}–C bond cleavage takes place. Sulphilimine with X = *o*-CO_2H due to neighbouring-group participation hydrolyses very rapidly via acyloxy-sulphurane and acyloxy-sulphonium ion intermediates with five-memembered ring (S_Ni reaction involving S^{IV}–N bond cleavage).

INTRODUCTION

N-Sulphonyl sulphilimines ($R^1R^2SNSO_2R^3$) are generally known to hydrolyse in moderately concentrated solutions of strong acids with S(IV)–N *bond cleavage* yielding sulphoxides (R^1R^2SO) and sulphonamides ($R^3SO_2NH_2$). In a previous paper[1] we have concluded that the conjugate acids of XC_6H_4(Me)SNTs and Ph(Me)$SNSO_2C_6H_4Y$ undergo a hydrolysis of S_N2 type in which water molecules act as both nucleophiles and proton-transfer agents. The reactivity of the protonated substrates is enhanced by electron-withdrawing X and Y groups. Later on, an optically active sulphilimine with X = *o*-CO_2H has been observed to hydrolyse with the retention of configuration suggesting that sulphoxide formation assisted anchimerically by *o*-CO_2H group proceeds via a cyclic acyloxysulphonium ion intermediate (double inversion).[2]

$PhCH_2OH$ and $PhSO_2NHSCH_2COOH$ were earlier[3,4] detected among the products of hydrolysis of $(PhCH_2)_2$SNTs and HO_2CCH_2(^{t}Bu)$SNSO_2Ph$, respectively, indicating that the given sulphilimines hydrolyse by a S(IV)–C *bond cleavage*. On the other hand, R^1R^2SNTs (R^1,R^2 = aryl or n-alkyl) dissolved in conc sulphuric acid is deacylated with the *cleavage of* the S(VI)–N *bond*.[5]

Since acid-catalysed sulphilimine hydrolysis may follow different courses, we have studied more extensively the dependence of rate on structure and acidity in order to obtain further information about its mechanisms. Two series of XC_6H_4(R)SNTs were investigated: S-phenyl-N-tosyl-sulphilimines (X = H) with different S-alkyl groups, R = Me (**1a**), Et (**1b**), Pr (**1c**), ^{i}Pr (**1d**), ^{t}Bu (**1e**), $PhCH_2$ (**1f**), and S-methyl-N-tosyl-sulphilimines (R = Me) with different S-aryl groups, X = *o*-CO_2H (**2a**), *o*-CO_2Me (**2b**), *o*-CH_2CO_2H (**2c**), *o*-CH_2CO_2Me (**2d**), *o*-Cl (**2e**), *o*-OMe (**2f**), *m*-CO_2H (**2g**), *m*-CO_2Me (**2h**), *p*-CO_2H (**2i**), *p*-CO_2Me (**2j**).

RESULTS AND DISCUSSION

In the solutions of mineral acids N-sulphonyl sulphilimines as moderately strong bases[6] suffer equilibrium protonation and the conjugate acids undergo a slow hydrolysis reaction.

$$R^1R^2\ddot{S}{=}\ddot{N}SO_2R^3 + H^+ \underset{K_a}{\rightleftharpoons} [R^1R^2\ddot{S}{=}\overset{+}{\ddot{N}}HSO_2R^3 \longleftrightarrow$$

$$R^1R^2\overset{+}{\ddot{S}}{-}\ddot{N}HSO_2R^3] \xrightarrow{H_2O} \text{Hydrolysis products.} \quad (1)$$

For sulphilimine hydrolysis, eqn (1) involves the pseudo-unimolecular rate-law (2) where k_ψ and $[S]_{st}$ represent the rate constant and the stoichiometric concentration of sulphilimine, respectively:

$$\text{rate} = k_\psi [S]_{st}. \quad (2)$$

The dependence of rate on acidity, temperature and substrate indicates how water participates in the rate-determining step, thus providing evidence for the different courses of sulphilimine hydrolysis.

Kinetic measurements were carried out at 25–60° in moderately concentrated (1–10 M) aqueous $HClO_4$ (solvent A) or in (0.5–6 M) 1:1 (v/v) EtOH/H_2O–$HClO_4$ (solvent B). Only solvent B was used when substrates and/or products were insoluble or too reactive in aqueous acid.

Rate-acidity profiles. As it was expected, the hydrolysis of XC_6H_4(R)SNTs proceeded according to eqn (2). The k_ψ values determined in solvents A and/or B of different acidities are listed in Table 1 (Table 4, too). For all these sulphilimines the dependence of k_ψ values on acidity was found to fit into one of three basic categories as shown in Fig. 1. Type A is characterized by a max at 3.0–3.2 M and it is typical for Ph(R)SNTs with R = n-alkyl (**1a-c**) and XC_6H_4(Me)SNTs with X = *o*-CO_2Me and *o*-CH_2CO_2H (**2b-c**). Type B is similar to a sigmoid curve and it is characteristic for the hydrolysis of Ph(R)SNTs with R = ^{i}Pr, ^{t}Bu and CH_2Ph (**1d–f**). Type C found for S-methyl-S-(2-carboxyphenyl) derivative (**2a**) resembles type B except that a decrease in rate occurs at higher at higher acidity (> 4 M). The data reported for **1a** and **1d** show that the shapes of the rate-acidity profiles are independent of the solvent used ($HClO_4$ in water or in water–ethanol).

The diversity of rate-acidity dependences indicates that the mechanisms of hydrolysis is not the same for all sulphilimines. The rate profiles A and B, similar to those observed for primary alkyl and t-butyl acetates,[7] respectively, seem to be correlated with hydrolysis reactions of S_N2 and S_N1 types (cf. the A-2 hydrolysis of carboxamides, too[8]).

The treatment of rate data in a more quantitative manner may give a stronger evidence for the mechanisms suggested by different rate profiles. Since the conjugate acids of sulphilimines are involved in the hydrolysis

Table 1. Hydrolysis rates for $XC_6H_4(R)SNTs$ in aqueous $HClO_4$ (solvent A) and in 1:1 (v/v) $EtOH/H_2O$–$HClO_4$ (solvent B)

Ia; X=H, R=Me Solvent B[a]; t=50°		Ib; X=H, R=Et Solvent A; t=50°		Ic; X=H, R=Pr Solvent A; t=50°		Id; X=H, R=^{i}Pr Solvent A; t=50°		Id; X=H, R=^{i}Pr Solvent B; t=50°	
$[HClO_4]$ M	$10^5 k_\psi$ (sec^{-1})	$[HClO_4]$ M	$10^6 k_\psi$ (sec^{-1})	$[HClO_4]$ M	$10^6 k_\psi$ (sec^{-1})	$[HClO_4]$ M	$10^5 k_\psi$ (sec^{-1})	$[HClO_4]$ M	$10^5 k_\psi$ (sec^{-1})
0,52	0.80	1.58	5,08	1.27	4.61	2.89	0,57	1,60	0.11
1,01	1.55	1.92	6.39	1.58	5.49	3.94	1.99	2.01	0.22
1.53	2.43	2.70	8,51	2.32	6.16	5.06	4.76	2.54	0.51
2.04	2.90	3.44	9.45	3.20	7.65	6.11	5.81	3.14	0.98
2.55	3.14	3.77	9.08	3.77	7.50	7.10	7.17	3.59	1.91
2.95	3.28	4.36	7.62	4.36	6.57	7.98	8.19	4.05	3.21
3.42	2.90	4.75	6.19	4.74	5.60	8.84	8.81	4.56	4.22
3.97	1.68	5.23	4.19			9.91	10.7	5.19	4.94
4.50	1.20							5.55	5.51

Ie; X=H, R=^{t}Bu Solvent B; t=20°		If; X=H, R=CH_2Ph Solvent B; t=25°		IIa; X=o-CO_2H, R=Me Solvent B; t=25°		IIb; X=o-CO_2Me, R=Me Solvent B; t=60°		IIc; X=o-CH_2CO_2H, R=Me Solvent B; t=50°	
$[HClO_4]$ M	$10^5 k_\psi$ (sec^{-1})	$[HClO_4]$ M	$10^5 k_\psi$ (sec^{-1})	$[HClO_4]$ M	$10^5 k_\psi$ (sec^{-1})	$[HClO_4]$ M	$10^5 k_\psi$ (sec^{-1})	$[HClO_4]$ M	$10^5 k_\psi$ (sec^{-1})
2.93	1.69	3.09	1.82	1.00	0.70	1.10	0.59	1.03	0.46
3.44	2.94	3.57	3.74	1.55	1.80	1.56	0.94	1.56	0.91
4.07	5.89	3.96	6.78	2.03	4.44	2.07	1.28	2.03	1.32
4.49	13.0	4.53	12.8	2.27	5.85	2.64	1.46	2.63	1.61
4.78	18.3	4.80	15.9	2.58	10.4	3.14	1.67	3.05	1.77
5.23	36.9	5.10	20.1	3.10	18.6	3.55	1.62	3.49	1.64
5.45	74.0	5.31	22.8	3.52	26.4	4.04	1.18	4.03	1.33
		5.47	25.3	4.00	30.1	4.52	0.70	4.47	0.69
				4.50	28.4	5.12	0.37	4.95	0.46
				5.08	22.7				
				5.62	17.2				

[a] k_ψ data measured in solvent A were published in a previous paper.[1]

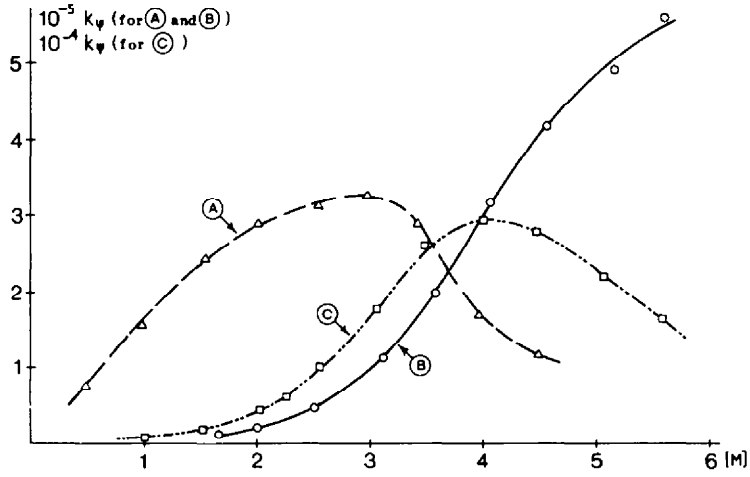


Fig. 1. The dependency of the rate on acidity for the hydrolysis of $XC_6H_4(R)SNTs$ in 1:1 (v/v) $EtOH/H_2O$–$HClO_4$ solutions; Ⓐ for Ph(Me)SNTs (**1a**; 50°); Ⓑ for Ph('Pr)SNTs (**1d**: 50°); Ⓒ for *o*-CO_2H–C_6H_4(Me)SNTs (**2a**; 25°).

reaction, the rates can also be expressed as a function of protonated substrate concentration (3).

$$\text{rate} = k_\psi [S]_{st} = k_p [SH^+] \quad (3)$$

$$k_p = k_\psi (h_X + K_{SH^+})/h_X. \quad (4)$$

Rate coefficient k_p is correlated with the experimental rate constant (k_ψ) by eqn (4) where h_X symbolizes the antilogarithm of $-H_X$ valid for the given sulphilimine base, and K_{SH^+} represents the thermodynamic acidity constant of the conjugate acid. These k_p values and their

dependence on solvent acidity will be taken into account when the relative reactivities of the protonated substrates and the role of water molecules in the rate-determining step are discussed. In order to evaluate k_p coefficients, pK_{SH^+} values were determined.

Basicity and acidity functions. For the determination of pK_{SH^+} constants of sulphilimines $\log [SH^+]/[S] = \log I$ values were measured by UV spectrophotometric method. Using these values, the acidity constants were calculated by Bunnett-Olsen's l.f.e.r. method[9] (5 and 6) and by the acidity function (a.f.) method [7] (7).

$$H_X + \log c_{H^+} = (1 - \Phi_e)(H_0 + \log c_{H^+}) \quad (5)$$

$$\log I + H_0 = \Phi_e(H_0 + \log c_{H^+}) + pK_{SH^+} \quad (6)$$

$$\log I + m H_0 = pK_{SH^+}. \quad (7)$$

Measurements for **1a-d** were carried out in solvent A at 25°. Φ_e, pK_{SH^+} and m data are collected in Table 2. (H_0 values were taken from lit.[10,11]). The same data for compounds **1a, d, f** and **2b-f** were determined in solvent B (Table 2; calculations were based on H_0 values reported for the same solvent[12]). The pK_{SH^+} data obtained by l.f.e.r. and a.f. methods agree well within the limits of experimental error. The Φ_e and pK_{SH^+} values measured by l.f.e.r. method were used for calculating H_X and k_p (cf. eqns 5 and 4) required for the quantitative treatment of rate data of sulphilimine hydrolysis (see later).

Since Ph('Bu)SNTs (**1e**) and *o*-CO_2H–C_6H_4(Me)SNTs (**2a**) are hydrolyzing rapidly even at 25° the pK_{SH^+} constants for these compounds cannot be determined by the above method. However, using pK_{SH^+} data of **1a, 1d** and **1f**, and the σ^* values of Me, 'Pr, CH_2Ph and 'Bu groups,[13] an approximate pK_{SH^+} value of −2.16 can be calculated for **1e** from the Taft-equation ($\Delta pK_{SH^+} = \rho^* \Delta\sigma^*$ with $\rho^* = 1.63$). The average of Φ_e parameters of **1a, 1d** and **1f** (−0.137) was used for **1e**. In the case of **2a**, the pK_{SH^+} value measured for the *o*-methoxy-carbonyl derivate (**2b**) was attributed to the *o*-carboxy derivative.

†The investigation of sulphilimine hydrolysis in the lower acidity region as well as the interpretation of results are now in progress and will be the subject of a next paper.

Both Φ_e and m parameters ($m \sim 1 - \Phi$) listed in Table 2 indicate that $XC_6H_4(R)SNTs$ sulphilimines behave nearly as Hammett-bases. Nevertheless, the negative Φ_e values show that the solvation requirements of acid-conjugated sulphilimines are somewhat lower than those of protonated Hammett-bases (cf. the interpretations suggested by Modena and Scorrano[14]). This can be attributed to the delocalization of the positive charge in $XC_6H_4(R)$-$\overset{+}{S}$NHTs having some sulphonium character.

$$\text{Aryl—}\overset{+}{\text{S}}\text{—}\ddot{\text{N}}\text{H—} \leftrightarrow \text{Aryl—S}{=}\overset{+}{\text{N}}\text{H—}$$

By comparing Φ_e values, it also follows that the behaviour of sulphilimines ($\Phi_e = -0.1$ to -0.2) in acid solutions differs significantly from that of analogous sulphoxides ($\Phi_e = +0.4$ to $+0.6$)[14]; cf. the Φ_e values of −0.26 to −0.29 found for sulphides.[14]

Quantitative treatment of rate data. Investigating the role of water molecules in the rate-determining step of sulphilimine hydrolysis we correlated k_p data (cf. eqns 4 and 5) with the acidity of the solvent by using Bunnett–Olsen's treatment[15] proposed for moderately basic substrates (8).

$$\log k_p = \Phi_r(H_0 + \log c_{H^+}) + \log k_p^0. \quad (8)$$

The Φ_r parameters and $\log k_p^0$ values relating to infinite solutions in solvents A and/or B were calculated and collected in Table 3.

By plotting k_p values determined for **1d-f** in solvent B against $H_0 + \log c_{H^+}$ we obtained curves going through max and showing linearity only beyond a relatively high acid concentration (~4.0 M). Consequently, solvation (and activation) parameters were calculated for the range 4.0–5.5 M.† (Using solvent A, **1d** was also investigated in a much wider concentration range, but practically the same solvation parameter was obtained in both cases.)

In order to compare directly the solvation requirements of different transition states developing in the hydrolysis of sulphilimines $\Phi_\pi = \Phi_r + \Phi_e$ values were also calculated as proposed by Modena and Scorrano[14] (Table 3).

Table 2. Solvation parameters and pK_{SH^+} values for $XC_6H_4(R)SNTs$ in aqueous $HClO_4$ (solvent A) and 1:1 (v/v) $EtOH/H_2O$-$HClO_4$ (solvent B) at 25°

	$XC_6H_4(R)SNTs$ X	R	Solvent	Wave length for determ. (nm)	l.f.e.r. method Φ_e	pK_{SH^+}(a)	a.f. method m	pK_{SH^+}(a)
Ia	H	Me	A	275	−0.17	−2.14	1.11	−2.18
Ia	H	Me	B	276	−0.15	−2.64	1.14	−2.66
Ib	H	Et	A	275	−0.19	−2.23	1.15	−2.27
Ic	H	Pr	A	281	−0.09	−2.08	1.08	−2.11
Id	H	^{i}Pr	A	281	−0.09	−2.08	1.07	−2.10
Id	H	^{i}Pr	B	278	−0.10	−2.34	1.08	−2.35
If	H	CH_2Ph	B	279	−0.16	−2.96	1.13	−2.99
IIb	o-COOH	Me	B	294	−0.14	−2.83	1.12	−2.86
IIc	o-CH_2COOH	Me	B	286	−0.17	−2.65	1.14	−2.67
IId	o-CH_2COOMe	Me	B	286	−0.11	−2.72	1.09	−2.74
IIe	o-Cl	Me	B	294	−0.20	−3.04	1.17	−3.09
IIf	o-OMe	Me	B	306	−0.20	−2.19	1.12	−2.22

(a) Standard deviation ±0.10

Table 3. Solvation parameters for the hydrolysis of $XC_6H_4(R)SNTs$ in aqueous $HClO_4$ (solvent A) and in 1:1 (v/v) EtOH/$HClO_4$ (solvent B)

$XC_6H_4(R)SNTs$ X	R	Solvent	t °C	Φ_r value of parameter	corr. coeff.	concentration range M	$10^5 k^o_{p_1}$ (sec^{-1})	$\Phi_\neq$
Ia[a] H	Me	A	50	+1.21	0.9998	1.00–5.79	218	+1.04
Ia H	Me	B	50	+1.16	0.9990	0.52–4.50	658	+1.01
Ib H	Et	A	50	+1.23	0.9998	1.58–5.23	61.0	+1.04
Ic H	Pr	A	50	+1.19	0.9983	1.27–4.74	44.4	+1.10
Id H	^{i}Pr	A	50	−0.08	0.9422	2.89–9.91	4.53	−0.17
Id H	^{i}Pr	B	50	−0.15	0.9559	3.59–5.55	1.85	−0.25
Ie H	^{t}Bu	B	20	−0.95	0.9892	4.07–5.45	0.07	−1.10
If H	CH_2Ph	B	25	−0.26	0.9968	4.53–5.47	3.88	−0.42
IIa o-CO_2H	Me	B	25	+0.41	0.9967	1.00–5.62	386	+0.27
IIb o-CO_2Me	Me	B	60	+1.05	0.9987	1.10–5.12	341	+0.91
IIc o-CH_2CO_2H	Me	B	50	+0.97	0.9987	1.03–4.95	189	+0.80

(a) k_ψ data measured in solvent A were taken from a previous paper[1]

By comparing Φ_r or $\Phi_\neq$ parameters of **Ia** and **Id** measured in solvents A and B it can be seen that they do not depend essentially on the ethanol content of the solvent used.

Activation parameters and relative reactivities. The dependence of rate constants k_ψ on temperature (generally 50, 55, 60°) was measured in solvents A and/or B of given acidity. The experimental data fit the Arrhenius equation. The activation parameters $\Delta H^\neq$ and $\Delta S^\neq$ (50°) evaluated from the equation $k_\psi = (kT/h) \exp(\Delta S^\neq/R) \exp(-\Delta H^\neq/RT)$ are given in Table 4. The reactivities of acid-conjugate sulphilimines can be compared by their relative rates of hydrolysis (k_{rel}) as listed in Table 4.

Product analysis. By polarographic analysis (cf. lit.[1]) it was established that $XC_6H_4(Me)SO$ sulphoxides were quantitatively formed from sulphilimines **1a-c** and **2a-j**. In the case of **1d-f** no sulphoxide was observed and only

Table 4. Activation parameters and relative rates for the hydrolysis of $XC_6H_4(R)SNTs$ in aqueous $HClO_4$ (solvent A) and in 1:1 (v/v) EtOH/H_2O–$HClO_4$ (solvent B) at 50°

$XC_6H_4(R)SNTs$ X	R	Solvent	$[HClO_4]$ M	$10^5 k_\psi$ (sec^{-1})	$\Delta H^\neq$ (kcal.mól^{-1})	$\Delta S^\neq$ (e.u.)	k_{rel}
Ia[a] H	Me	A	2.00	2.89	19.5	−19.0	1[b]
Ia H	Me	B	2.06	2.90	18.9	−22.3	1[c]
Ib H	Et	A	3.44	0.95	18.7	−23.7	0.28[b]
Ic H	Pr	A	4.36	0.66	18.4	−25.4	0.20[b]
Id H	^{i}Pr	A	7.98	8.19	25.4	+1.3	0.02[b]
Id H	^{i}Pr	B	4.03	3.24	25.0	−2.0	1.42[c]
Ie H	^{t}Bu	B	4.03	152[d]	19.9	−10.0	65.8[c,d]
If H	CH_2Ph	B	4.03	127[d]	23.0	−0.73	91.1[c,d]
IIa o-CO_2H	Me	B	2.06	67.4	19.9	−11.6	38[c]
IIb o-CO_2Me	Me	B	2.06	0.33	17.4	−28.9	0.27[c]
IIc o-CH_2CO_2H	Me	B	2.06	1.31	17.4	−27.2	0.45[c]
IId o-CH_2CO_2Me	Me	B	2.06	1.32	17.8	−25.0	0.57[c]
IIe o-Cl	Me	B	2.06	2.96	19.0	−20.7	2.22[c]
IIf o-OMe	Me	B	2.06	1.76	18.5	−23.2	0.21[c]
IIg m-CO_2H	Me	B	2.06	5.91	18.8	−19.9	2.04[e]
IIh m-CO_2Me	Me	B	2.06	6.39	18.2	−21.5	2.20[e]
IIi p-CO_2H	Me	B	2.06	5.01	18.6	−20.6	1.73[e]
IIj p-CO_2Me	Me	B	2.06	5.69	16.6	−26.6	1.96[e]

(a) Data were taken from a previous paper.[1]

(b) Calculated from data determined in solvent A and extrapolated to infinite dilution by using equation $k_{rel} = k^o_p$ (substrate)/k^o_p (Ia)

(c) Calculated from data determined in solvent B of given acidity by using equation $k_{rel} = k_p$(substrate)/k_p (Ia). For Ia $k_p = 79.4 \times 10^{-5}$ and 2.64×10^{-5} sec^{-1} values determined in $HClO_4$ solutions of 2.06 M and 4.03 M, respectively, were taken into account.

(d) k_p(substrate) value at 50° was calculated from k_ψ value measured at 20° (Ie) or 25° (If) and extrapolated by the Arrhenius equation.

(e) Because of failure to determine pK_{SH^+} by UV method, $k_{rel} = k_\psi$(substrate)/k_ψ (Ia) values are given.

$TsNH_2$, PhSSPh and $PhSSO_2Ph$ were determined in the chloroform extract of the mixture by IR spectroscopic method. ^tBuOH and $PhCH_2OH$ formed from **1e** and **1f**, respectively, were detected by NMR spectroscopic method.

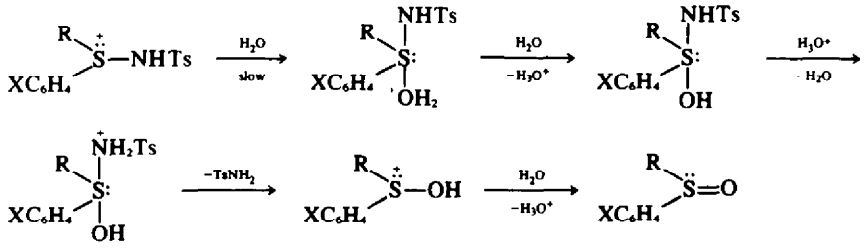
Mechanisms. The acid-catalyzed hydrolysis of **1a-c** and **2b-c** exhibiting a rate-acidity profile of *type A* can be characterised by a Φ_r value within the range from +0.97 to +1.23 (Table 3). This corresponds to a high degree of participation of water molecules in the reaction. According to Bunnett–Olsen's classification,[15] in this case water acts not only as a nucleophile but also as a proton-transfer agent in the rate-determining step. Thus, the conjugate acids of these compounds seems to follow *course A* when undergoing hydrolysis in moderately strong acidic solutions. The reaction of the S_N2 type starts with the nucleophilic addition of water on sulphur atom producing a sulphurane intermediate,[16] and it is promoted by acid-base catalysis.

For the hydrolysis of **1d-f** having a rate-acidity profile of *type B*, negative Φ_r values within the range from −0.95 to −0.08 were observed in solutions of relatively high (4–5.5 M) acid concentration (Table 3). According to Bunnett–Olsen's classification[15] it may be assumed that water does not take part in the rate-determining step. Consequently, the hydrolysis of the acid conjugates of Ph(R)SNTs with R = ^iPr, ^tBu and CH_2Ph groups presumably follows *course B* (S_N1 mechanism) which is promoted by the relative stability of R^+ carbenium ion.

The negative Φ_r values for **1d-f** (from −1.10 to −0.17) are obviously due to the rather low solvation requirements of the carbenium centre developing in the transition state (cf. lit.[14]).

$\Delta H^{\neq}$ and $\Delta S^{\neq}$ data shown in Table 4 also indicate that a change in mechanism (S_N1 instead of S_N2) occurs if the R group in Ph(R)SNHTs is bulky and can split as a relatively stable carbenium ion. As expected, the order of reactivities in the S_N1 reaction is $^iPr < CH_2Ph$, ^tBu.

Course A



Φ_x values for **1a-c** and **2b-c** (from +0.80 to +1.10) indicate that in the transition state an oxonium centre with high solvation requirements is developed by the nucleophilic attack of water on a sulphonium centre having relatively low solvation requirements (cf. lit.[14]).

The activation parameters of **1a-c** and **2b-j** (Table 4) indicate undoubtedly that sulphilimines Ph(R)SNTs with R = Me, Et and Pr, and all compounds of XC_6H_4(Me)SNTs type (except **2a** with X = *o*-CO_2H) undergo a bimolecular hydrolysis in acid solutions. The reactivity of the conjugate acids of **1a-c** decreases with increasing steric and +I effects of R substituents. Relative rates observed for **2e** and **2f** may be interpreted (cf. lit.[1]) semiquantitatively by different polar and steric effects[13] of X = *o*-Cl and *o*-MeO groups. (The positive ρ^* value is approximately in the range 1.6–1.9.) Compound **2b** with electron-withdrawing X = *o*-CO_2Me group, however, exhibits an unusual slow hydrolysis rate obviously due to a considerable steric hindrance (cf. **2g-j**). Furthermore, the proximity of the carbonyl–oxygen of *o*-CO_2Me group to the positively charged S atom may also inhibit the nucleophilic attack of water molecules.

Course A is also supported by the quantitative determination of sulphoxides formed from **1a-c** and **2b-j**.

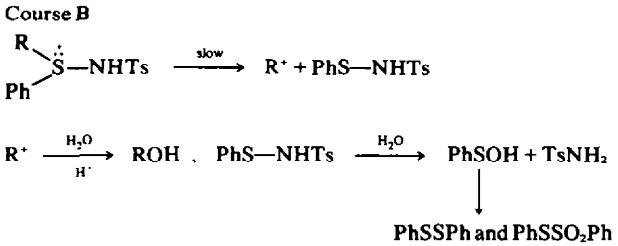
Intermediates R^+ and PhSNHTs formed by the unimolecular cleavage of the protonated substrate are unstable and undergo further hydrolysis in the solvent. R^+ reacts with water yielding alcohol. PhSNHTs hydrolyses to give $TsNH_2$ and PhSOH[17] from which PhSSPh and $PhSO_2SPh$ are formed.[18,19] The S_N1 mechanism proposed for the hydrolysis of **1d-f** has also been confirmed by the identification of the products mentioned. Although PhSSPh and $PhSSO_2Ph$ may also be formed from Ph(^tBu)SO by acid-catalysed hydrolysis,[19] the reaction rates invariably show that the primary hydrolysis product of **1e** cannot be a sulphoxide.

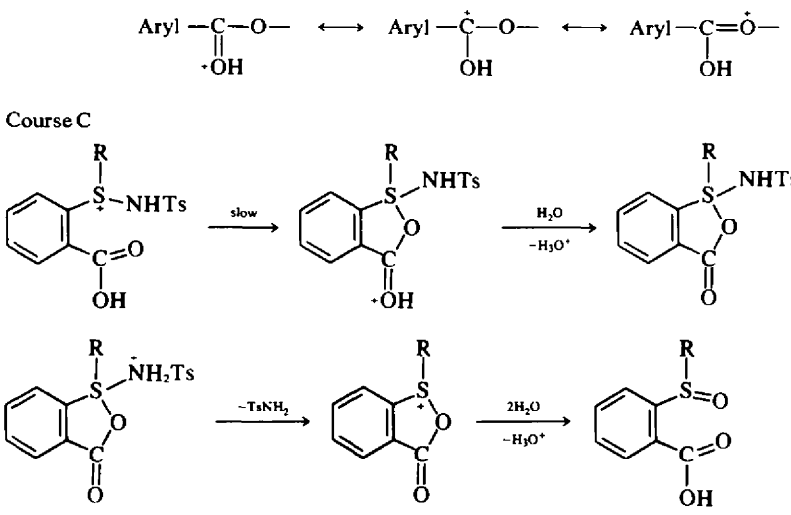
The rate-acidity profile of *type C* and $\Phi_r = +0.41$ observed for *o*-CO_2H–C_6H_4(Me)SNTs (**2a**) may be explained by a reaction scheme given as *course C* similar to that reported by Bohman and Allenmark[2] (S_Ni and S_N2 reactions promoted by acid–base catalysis). In the starting steps water acts as a base-catalyst and not as a nucleophile.

The medium high positive Φ_x value (+0.27) can be interpreted by the medium solvation requirements of the oxonium-carbenium moiety evolving in the transition state; cf. lit.[14]

The extremely high rate measured for the hydrolysis of **2a** can be well explained by the neighbouring-group

Course B





participation of *ortho* carboxy-group. The value of $\Delta S^{\neq}$ (−11.6 e.u.) can be correlated with an unimolecular reaction involving ring closure. On the other hand, the rate data found for **2c** show that *o*-CH_2CO_2H group has no significant rate-accelerating effect on sulphilimine hydrolysis, suggesting that the reaction yielding a cyclic acyloxy-sulphurane with a six membered ring is not favourable.

On the basis of all this, it has been concluded that the hydrolysis of $XC_6H_4(R)SNTs$ sulphilimines in moderately concentrated acidic solutions may follow different courses depending on what R and X groups they have. S_N2, S_N1 and $S_Ni + S_N2$ displacements established for the acid-catalyzed reactions of analogous $XC_6H_4(R)SO$ sulphoxides (cf. lit.[14,20]).

EXPERIMENTAL

Materials. The purity of compounds used in the kinetic measurements were checked by analysis and/or spectroscopic methods. Physical data (m.p., IR) characteristic for $XC_6H_4(R)SNTs$ sulphilimines are given in Table 5. IR spectra were recorded on a Zeiss UR-10 instrument in KBr pellets. M.ps were determined by a "Boetius" m.p. apparatus.

S - *t* - *Butyl* - S - *phenyl* - N - p - *tolylsulphonyl* - *sulphilimine* (**1e**). This compound was prepared by the method published earlier[21] with the modification that $TsNClNa{\cdot}2H_2O$ (13.2 g; 0.05 mol) was added in small portions to a cold (0°) soln of t-butyl-phenyl-sulphide (8.3 g, 0.05 mol) in abs MeOH (200 ml); yield 13 g (80%).

S - *Methyl* - S - (2 - *carboxyphenyl*) - N - p - *tolylsulphonyl* - *sulphilimine* (**2a**. This compound was prepared from (2-carboxyphenyl) - methyl - sulphide and anhydrous chloramine-T (98% of purity checked by iodometric titration) in abs dioxan by a method similar to that of Bohman *et al.*[2] Finally powdered $TsNClNa{\cdot}2H_2O$ was desiccated in vacuum over P_2O_5 for 6 days at room temp. The reaction was carried out at 20°. The crude product was recrystallized from abs MeOH (60%).

S - *Methyl* - S - *methoxycarbonylphenyl* - N - p - *tolylsulphonyl* - *sulphilimines* (**2b**, **2h**, **2j**). The reaction of **2a**, **2g** and **2i** with diazomethane carried out by the usual method gave methyl esters in nearly quantitative yields. The crude products were recrystallized from abs MeOH. (Found: C, 54.8; H, 5.0; N, 3.9; S, 18.0 for *ortho*-isomer; C, 54.6; H, 4.9; N, 4.0; S, 17.9 for *meta*-isomer; C, 54.6; H, 5.0; N, 3.8; S, 17.9 for *para*-isomer. Calc. for $C_{16}H_{17}NO_4S_2$ (351.5): C, 54.7; H, 4.9; N, 4.0; S, 18.3%).

Table 5. Data for $XC_6H_4(R)SNTs$ used in kinetic experiments

	$XC_6H_4(R)SNTs$ X	R	IR data $\nu_{as(SO_2)}$ cm^{-1}	$\nu_{s(SO_2)}$ cm^{-1}	$\nu_{as(SNS)}$ cm^{-1}	$\nu_{s(SNS)}$ cm^{-1}	m.p. °C	Preparation
Ia	H	Me	1281[21]	1145[21]	935[21]	747	132	lit.[22]
Ib	H	Et	1280[21]	1141[21]	978[21]	760	99-100	lit.[23]
Ic	H	Pr	1284[21]	1143[21]	979[21]	760	85-86	lit.[24]
Id	H	^{i}Pr	1284[21]	1149[21]	950[21]	758	116,5-117	lit.[21]
Ie	H	^{t}Bu	1298	1147	961	760	107-108 (decomp.)	exp.part
If	H	CH_2Ph	1281	1139	991, 968	747, 754	136-137	lit.[25]
IIa	o-COOH	Me	1279	1139	944	762	125,5-126	exp.part
IIb	o-COOMe	Me	1280	1142	946	770, 762	164,5-165	exp.part
IIc	o-CH_2COOH	Me	1289	1143	948	772	168,5-170	exp.part
IId	o-CH_2COOMe	Me	1280	1141	941	762	138,5-139,5	exp.part
IIe	o-Cl	Me	1294, 1280	1142	949, 940	770, 760	145-145,5	exp.part
IIf	o-OMe	Me	1293, 1280	1141	938[23]	770, 751	100-101	lit.[22]
IIg	m-COOH	Me	1271	1141	950[23]	756	177	lit.[26]
IIh	m-COOMe	Me	1290	1150	960	762	145-145,5	exp.part
IIi	p-COOH	Me	1284	1141	961	751	192-193	lit.[27]
IIj	p-COOMe	Me	1287	1141	980	760	167,5-168	exp.part

S - *Methyl* - S - (2 - *methoxycarbonylmethyl* - *phenyl*) - N - p - *tolylsulphonyl* - *sulphilimine* (**2d**). 2 - Methylthio-phenyl acetic acid[29] (2.73 g, 15 mmol) suspended in abs MeOH (25 ml) was treated in the usual way with diazomethane dissolved in ether. The solvent was removed under reduced pressure. The oily residue was dissolved in a mixture of abs dioxan (40 ml) and AcOH (1 ml) then $TsNClNa \cdot 2H_2O$ (3.95 g, 15 mmol) was added. The mixture was stirred for 8 hr at room temp. The solvent was removed under reduced pressure and the residue triturated with cold 5% NaOH aq (20 ml). The crystals were filtered, washed with cold water, and crystallized from MeOH (25 ml) without drying; yield 3.6 g (60%). (Found: C, 56.0; H, 5.3; N, 3.8; S, 17.6. Calc. for $C_{17}H_{19}NO_4S_2$ (365.4): C, 55.9; H, 5.2; N, 3.8; S, 17.6%).

S - *Methyl* - S - (2 - *carboxymethyl* - *phenyl*) - N - p - *tolylsulphonyl* - *sulphilimine* (**2c**). NaOH (0.24 g, 6 mmol) dissolved in water (5 ml) was added to **2d** (1.1 g, 3 mmol) suspended in MeOH (10 ml). The mixture was stirred for 1 hr at room temp.; then the soln was concentrated to a small volume by evaporation and diluted with water (3 ml). After acidifying by 2N H_2SO_4 aq, the ppt was filtered, washed with cold water and desiccated in vacuum over P_2O_5; yield 0.97 g (100%). (Found: C, 54.6; H, 5.0; N, 4.0; S, 18.3. Calc. for $C_{16}H_{17}NO_4S_2$ (351.4): C, 54.7; H, 4.9; N, 4.0; S, 18.3%).

S - *Methyl* - S - (2 - *chlorophenyl*) - N - p - *tolylsulphonyl* - *sulphilimine* (**2e**). This compound was prepared from (2-chloro - phenyl) - methyl - sulphide and chloramine-T by the general method published earlier.[28] The crude product was recrystallized from EtOH; yield 52%. (Found: C, 51.4; H, 4.4; Cl, 11.0; N, 4.2; S, 19.4. Calc. for $C_{14}H_{14}ClNO_2S_2$ (327.9): C, 51.3; H, 4.3; Cl, 10.8; N, 4.3; S, 19.6%).

pK_{SH^+} measurements. pK_{SH^+} data of sulphilimines listed in Table 2 were determined in aqueous (1–70%) $HClO_4$ and/or in 1:1 (v/v) $EtOH/H_2O$–$HClO_4$ (1–35% $HClO_4$) by UV spectrophotometric method. The stock solutions of sulphilimines (10^{-4}–4×10^{-4} M) were made immediately before running the spectra. Absorptions at the given wave lengths were recorded at 25° on a Beckman Model DU instrument.

The sigmoid plots of absorbances (A) against acidity indicated that the absorbances of sulphilimine bases (A_B) were not affected by the acidity of the solvent, whereas those of the conjugate acids (A_{BH^+}) were linear functions of H_0 ($A_{BH^+} = a + bH_0$); cf. lit.[30,31] Taking this into consideration, pK_{SH^+} values were computed (least squares method) by using the equation $\log I = \log (A - A_B)/A_{BH^+} - A$), eqns (6) and (7).

Kinetics. Hydrolysis rates were measured by the polarographic method used in our earlier experiments.[1] The measurements were accurate to within ±5% Φ_r, k_p^o, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values were computed by iteration (least squares method).

Product analysis (hydrolysis of **1d-f**). Sulphilimine (10 mmol) was stirred in 2 N (for **1e**, **1f**) or in 5.2 N (for **1d**) $HClO_4$ aq (50 ml) up to 100% conversion of the substrate (about 60 hr). Sulphilimine dissolved slowly, later the clear soln became turbid from products formed. After complete hydrolysis the concentration of $HClO_4$ was diminished to 0.1 N by adding 2 N NaOH aq to the mixture. Products were extracted by chloroform (3 × 30 ml). From the chloroform extract (dried over $MgSO_4$ sicc) the solvent was removed under reduced pressure. The products in the residue were determined by both NMR and IR spectroscopic methods.

NMR spectroscopic method. The crude products obtained by the hydrolysis of **1d-f** were dissolved in $CDCl_3$ and NMR spectra were taken on a ZKR 60 apparatus (Zeiss, Jena). NMR spectra of $C_6H_5(R)SNTs$, $C_6H_5(R)SO$ and ROH with R = 'Pr, 'Bu and $C_6H_5CH_2$ were also recorded. The signals suitable for the identification of products are given in Table 6.

Data in Table 6 show that only 'BuOH (from **1e**) and $C_6H_5CH_2OH$ (from **1f**) and no sulfoxide can be detected. 'PrOH as a volatile hydrolysis product of **1d** cannot be identified by this method.

IR spectroscopic method. The crude products obtained by the hydrolysis of **1d-f** were treated with a solvent-system 10:1 (v/v) hexane-ether. The insoluble product was identified as *p*-toluenesulphonamide by its IR spectrum. After evaporation the soluble products were dissolved in chloroform and IR spectra were taken. By this method PhSSPh and $PhSO_2SPh$ were also identified as hydrolysis products of **1d-f**. Characteristic frequencies are: for PhSSPh $\nu(C_Ar C_Ar)$: 1579, 1479, 1440 cm^{-1}; $\delta(C_Ar H)$: 1078, 1023 cm^{-1}; $\gamma(C_Ar C_Ar)$: 693 cm^{-1}; for $PhSO_2SPh$ $\nu(C_Ar C_Ar)$: 1582, 1478, 1448 cm^{-1}; $\nu(SO_2)$: 1329, 1313, 1147 cm^{-1}; $\delta(C_Ar H)$: 1078, 1023 cm^{-1}; $\gamma(C_Ar C_Ar)$: 690 cm^{-1}; $\delta(SO_2)$: 595, 538 cm^{-1}.

Table 6. Characteristic signals for $C_6H_5(R)SNTs$, $C_6H_5(R)SO$ and ROH[a]

Compound	R = $C(CH_3)_3$ $\delta(CH_3)$	R = $C_6H_5CH_2$ $\delta(CH_2)$	R = $CH(CH_3)_2$ $\delta(CH)$
$C_6H_5(R)SNTs$	1.25	4.24	3.21
$C_6H_5(R)SO$	1.19	4.07	2.85
ROH	1.28	4.61	3.99
Product	1.27	4.64	-

[a]Internal standard TMS

PhSSPh/$PhSO_2SPh$ product-distribution was determined on the basis of significant difference in the intensities of bands at 1078 and 1023 cm^{-1}. The amount of $PhSO_2SPh$ could also be determined by measuring the intensity of the band at 1147 cm^{-1}. Absorption coefficients are: for PhSSPh $a_{1023} = 4.54 \times 10^{-3}$; $a_{1078} = 5.78 \times 10^{-4}$; $a_{1147} = 0$; for $PhSO_2SPh$ $a_{1023} = 1.96 \times 10^{-3}$; $a_{1078} = 8.02 \times 10^{-3}$; $a_{1147} = 3.06 \times 10^{-2}$ (solvent: $CHCl_3$; concentration: 1 g/l; cell length: 0.1 mm).

In the products of the hydrolysis of 1 mmol of **1d**, **1e** and **1f** 0.96, 0.94 and 0.88 mmol of $TsNH_2$, 0.21, 0.09 and 0.20 mmol of PhSSPh and 0.21, 0.16 and 0.12 mmol of $PhSO_2SPh$ were measured.

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