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BASICITY OF S(IV)N(sp^2)S(VI) GROUP IN N-SULPHONYL SULPHILIMINES

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Abstract—The extent of protonation of several N-sulphonyl sulphilimines of $XC_6H_4(Me)SNTs$ and $MePhSNSO_2C_6H_4Y$ type has been measured in aqueous sulphuric acid by the UV technique. Sulphilimines follow the H_0 acidity function and thermodynamic pK_a's can be calculated from the equation given for Hammett-bases. The pK_a's range from $-1{\cdot}81$ (X = *p*-OMe) to $-3{\cdot}00$ (Y = *p*-NO_2). Structural effects on the basicity of the SNS group are similar to those of the SO group in sulphoxides. The Hammett ρ values for substituted sulphilimines are $\rho_X = +0{\cdot}89$ and $\rho_Y = +0{\cdot}82$. The basicities of sulphilimines are discussed and compared to those of nitrogen(sp^2) bases and other sulphur compounds.

INTRODUCTION

AS SHOWN earlier[1] by X-ray studies and MO calculations, the SN bonds of the S(IV)N(sp^2)S(VI) group in N-sulphonyl sulphilimines are of intermediate bond order ($R^1R^2S\overset{\cdots}{-}\dot{N}\overset{\cdots}{-}SO_2R^3$). The $S^{IV}N$ and $S^{VI}N$ bond lengths (1·63 and 1·58–1·60 Å, resp.) and the SNS bond angle (113–116°) in N-sulphonyl sulphilimines may be interpreted by the delocalization of two 2p electrons of the sp^2 N atom towards the neighbouring S atoms with empty 3d orbitals. It has also been pointed out that the preferred conformation of N-sulphonyl sulphilimines in the crystalline state seems to be controlled by the oriented lone pair of the sp^2 N atom.

Nevertheless, the possibility of the delocalization of the lone pair towards the neighbouring S^{VI} and S^{IV} atom cannot be neglected, either. From the $S^{IV}N$ and $S^{VI}N$ bond lengths (1·64 and 1·68 Å, resp.) found by Cook *et al.*[2] for an N-ethyl sulphiliminium salt of $[R^1R^1S\overset{\oplus}{N}(Et)SO_2Ar]X^{\ominus}$ type one may conclude that the relatively strong $S^{VI}N$ bond in N-sulphonyl sulphilimines (1·58–1·60 Å) is due not only to an $S^{IV}\overset{\cdots}{-}\dot{N}\overset{\cdots}{-}S^{VI}$ mesomeric structure, but to the delocalization of the lone pair, as well. Since the basicities of N-sulphonyl sulphilimines seem also to be controlled by the lone-pair delocalization, it is of theoretical interest to investigate the N-protonation reaction of the $S^{IV}NS^{VI}$ group, and to compare the basicities of N-sulphonyl sulphilimines with other nitrogen bases and sulphur compounds.

Very little is known concerning the basicity of sulphilimines. Briscoe[3] reported the preparation of S,S-dibenzyl-N-*p*-tolyl sulphonyl-sulphilimine hydrochloride* in 1953. Later, Andersen *et al.*[4] determined pK_a values for sulphoxides and some sulphilimines by titration in acetic anhydride with perchloric acid (pK_a's for Me_2SNTs, Ph_2SNTs and MePhSNTs were $+0{\cdot}57$, $-3{\cdot}60$ and $-1{\cdot}96$, resp.). This

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* N-protonation and d_π–p_π bond delocalization in the SNS group of this salt have been detected by its IR spectrum: ν(NH): 2650–2200, $\nu_{as}(SO_2)$: 1350, $\nu_s(SO_2)$: 1172, ν_{as}(SNS): 920 cm^{-1} (unpublished results of our laboratory).

method does not seem to be valid for the determination of thermodynamic pK_a's and was criticised by Landini *et al.*[5]. More recently, a value of pK_a = −1·78 was obtained for S-methyl-S-(4-methoxyphenyl)-N-*p*-tolylsulphonyl-sulphilimine by Tsujihara *et al.*[6] using the UV technique. On comparing the pK_a value of this compound with that of *p*-toluenesulphonamide, Tsujihara *et al.* concluded that "the electron density on the N atom is increased in the form of a coordination of the lone pair of the S-atom to the N atom".

While studying acid-catalysed sulphilimine hydrolysis[7] we were interested in the determination of pK_a values for sulphilimines of $XC_6H_4(Me)SNTs$ and $MePhSNSO_2C_6H_4Y$ type. Sulphilimines listed in Tables 1 and 2 were prepared and the extent of protonation in aqueous sulphuric acid solutions was measured.

RESULTS AND DISCUSSION

Determination of pK_a's *for* $XC_6H_4(Me)SNTs$ *and* $MePhSNSO_2C_6H_4Y$ *sulphilimines.* The pK_a's for the conjugate acids of sulphilimines as listed in Tables 1 and 2 were determined in aqueous sulphuric acid (1–80% H_2SO_4) by a UV spectrophotometric method. We have found the extinction of sulphilimines to differ quite significantly at a given wave-length from that of protonated bases, and the extinction of the deprotonated species (E_s) in extremely diluted acid solutions to be independent of acid concentration, similarly to that of protonated species (E_{SH^+}) in concentrated acid solutions. The plots of extinctions measured in 1–80% aqueous sulphuric acid *vs* H_0 are of sigmoid type. Knowing the values of E_S and E_{SH^+}, the ionization ratio ($[SH^+]/[S]$) can be calculated from measured extinctions (E) by using the formula $(E - E_S)/E_{SH^+} - E)$. The plots of log $[SH^+]/[S]$ *vs* H_0 have been found to be linear with a unit slope-parameter. Thus, sulphilimines behave as Hammett-bases, and thermodynamical pK_a's can be calculated from the correlation p$K_a = H_0 +$ log $[SH^+]/[S]$. Thermodynamical pK_a's for some $XC_6H_4(Me)SNTs$ and $MePhSNSO_2C_6H_4Y$ sulphilimines are given in Tables 1 and 2.

TABLE 1. pK_a VALUES FOR $XC_6H_4(Me)SNTs$ SULPHILIMINES

$XC_6H_4(Me)SNTs$		λ (mμ) Wavelength for detn.	log ε_λ		pK_a[d]	Preparation
X	σ_X[a]		Unprotonated species[b]	Protonated species[c]		
p-OMe	−0·268	273	3·57	3·96	−1·81	lit.[14]
H	0	278	2·59	3·17	−2·23	lit.[14]
m-OMe	+0·115	306	2·39	3·30	−2·26	lit.[14]
p-Cl	+0·227	267	3·29	3·64	−2·39	lit.[15]
m-Cl	+0·373	289	2·57	3·07	−2·48	exp. part
m-NO_2	+0·710	225	4·22	4·33	−2·85	lit.[14]
p-NO_2	+0·778	290	3·71	3·46	−2·93	lit.[14]

[a] The values of σ_X are taken from McDaniel and Brown's compilation.[13]

[b] Determined in water containing H_2SO_4 (<1M).

[c] Determined in 10M H_2SO_4.

[d] Standard deviation of the pK_a values is ±0·09.

pK_a Data of sulphilimines (pK_a's lie between −1·81 and −3·00) show that the basicity of the $S^{IV}{=}\ddot{N}{=}S^{VI}$ group in sulphilimines is much weaker than that of the $C(sp^2){=}\ddot{N}{=}C(sp^2)$ group (e.g. in pyridine). The significant difference in basicity is probably due to the delocalization of the lone pair (belonging to nitrogen) towards the neighbouring S^{VI} (and S^{IV}) atom with 3d orbitals in the sulphilimine group. The decreased basicities of sulphonamides may also be interpreted by a lone-pair delocalization. Nevertheless, N-sulphonyl sulphilimines proved to be somewhat stronger bases than sulphonamides ($pK_a = -2{\cdot}23$ and $-3{\cdot}30$ for MePhSNTs and $TsNH_2$[8], resp.). The difference in basicity is obviously due to the relative stability of the protonated bases. Indeed, a comparison of the protonated sulphilimines and sulphonamides shows that the positive charge of the 3-coordinated nitrogen of protonated N-sulphonyl sulphilimines is well delocalized on the $[S^{IV}{=}NH{=}S^{VI}]^{\oplus}$ moiety, with a d_π–p_π bond system while a similar delocalisation is not possible in protonated sulphonamides with a 4-coordinated nitrogen ($R—SO_2—\overset{+}{N}H_3$).

TABLE 2. pK_a VALUES FOR $MePhSNSO_2C_6H_4Y$ SULPHILIMINES

$MePhSNSO_2C_6H_4Y$		λ (mμ) Wavelength for detn	log ε_λ		pK_a[d]	Preparation
Y	σ_Y[a]		Unprotonated species[b]	Protonated species[c]		
p-OMe	−0·268	263	3·49	3·81	−2·13	exp. part
p-Me	−0·170	278	2·59	3·17	−2·23	lit.[14]
H	0	278	2·49	3·17	−2·36	exp. part
p-Cl	+0·227	281	2·37	3·07	−2·55	exp. part
p-NO_2	+0·778	292	3·79	3·43	−3·00	lit.[10]

[a] The values of σ_Y are taken from McDaniel and Brown's compilation.[13]
[b] Determined in water containing H_2SO_4 (< 1M).
[c] Determined in 10M H_2SO_4.
[d] Standard deviation of the pK_a values is ±0·09.

Furthermore, it is not surprising either that N-sulphonyl sulphilimines, in which a strong electron-withdrawing acyl group is attached to a N atom with an $S^{IV}N$ d_π–p_π bond, are weaker bases than sulphoximines, and not stronger than sulphoxides ($pK_a = -2{\cdot}23$, $+2{\cdot}73$ and $-2{\cdot}27$ for MePhSNTs, MePhS(NH)O[9] and MePhSO[5], resp.).

Substituent effect of X *and* Y *groups in the protonation of sulphilimines of* $XC_6H_4(Me)SNTs$ *and* $MePhSNSO_2C_6H_4Y$ *type*. The Hammett-plots of log K/K_0 *vs* σ_X (*cf* Table 1) and/or *vs* σ_Y (*cf* Table 2) are linear with a $\rho_X = +0{\cdot}89$ (r = 0·992) and $\rho_Y = +0{\cdot}82$ (r = 1·00), resp. From these ρ values it follows that the substituent effect of X and Y groups on the basicity of the S(IV)NS(VI) group is transmitted by —S(Me)= and —SO_2— groups, resp. The ρ's found for sulphilimine protonation are similar to those for other reactions of sulphur compounds (cf. $\rho = 0{\cdot}85$ for the protonation of aryl methyl sulphoxides[5] or $\rho_X = 1{\cdot}19$ and $\rho_Y = 1{\cdot}00$ for acid-catalysed sulphilimine hydrolysis[7]).

EXPERIMENTAL

Preparation of chloramines. Chloramines of $p\text{-}YC_6H_4SO_2NClNa$ type were used for the preparation of sulphilimines listed in Tables 1 and 2. Chloramine-T and chloramine-B (Y = Me or H) were commercial products of analytical purity. Chloramine-N ($Y = NO_2$) was prepared by a known method.[10]

Chloramine-Cl (Y = Cl). NaOH (4 g; 0·1 mole) and 4-chlorobenzene-sulphonamide (19·5 g; 0·1 mole) were dissolved in water (40 ml). The flask was cooled and 35 ml cold 3M NaOCl soln was added. Next day the crude product was filtered, washed with a small amount of water, recrystallized from water (50 ml) and dried over $CaCl_2$ in vacuum; yield 17 g (60%). The active chlorine content (99·4%) of the pure product ($p\text{-}ClC_6H_4SO_2NClNa.2H_2O$) was determined by iodometric titration.

Chloramine-M (Y = OMe). This compound was prepared similarly to chloramine-Cl, using 4-methoxybenzenesulphonamide as starting material; yield 51%. The active chlorine content of the pure product ($p\text{-}MeOC_6H_4SO_2NClNa.2H_2O$) was 99·5%.

Preparation of sulphilimines. Sulphilimines of analytical purity as listed in Tables 1 and 2 were prepared from appropriate chloramines and sulphides either by known methods (*cf* Tables) or by the following general procedure. The mixed solns of 0·03 mole of sulphide (in 45 ml of dioxane) and of 0·031 mole of chloramine (in 20 ml of water) were heated in water bath for 2 hr. Evaporation in vacuum gave an oily residue which was triturated with 20 ml of cold 5% NaOH aq and 10–15 ml ether (or toluene) until solidified completely. The crude product was filtered, washed thoroughly with water, dried and recrystallized from EtOH or MeOH (once or twice).

S-*Methyl*-S-(3-*chlorophenyl*)-N-p-*tolylsulphonyl-sulphilimine*. The recrystallized product was obtained by the general procedure outlined above; yield 47%; m.p. 133·5–134·5°; IR (KBr): $\nu_{as}(SO_2)$: 1278 cm^{-1}, $\nu_s(SO_2)$: 1141 cm^{-1}, $\nu_{as}(SNS)$: 950 cm^{-1}. (Found: C, 51·3; H, 4·4; N, 4·4; Cl, 11.1; S, 19·7. Calc. for $C_{14}H_{14}ClNO_2S_2$ (327·86): C, 51·3; H, 4·3; N, 4·3; Cl, 10·8; S, 19·6%).

S-*Methyl*-S-*phenyl*-N-*phenylsulphonyl-sulphilimine*. The recrystallized product was prepared by the general procedure; yield 59%; m.p. 87·5–88·0°; IR (KBr): $\nu_{as}(SO_2)$: 1288 cm^{-1}, $\nu_s(SO_2)$: 1140 cm^{-1}, $\nu_{as}(SNS)$: 958 cm^{-1}. (Found: C, 55·8; H, 4·7; N, 5·0; S, 23·1. Calc. for $C_{13}H_{13}NO_2S_2$ (279·39): C, 55·9; H, 4·7; N, 5·0; S, 23·0%).

S-*Methyl*-S-*phenyl*-N-(4-*chlorophenylsulphonyl*)-*sulphilimine*. The product recrystallized from MeOH was obtained by the general procedure; yield 65%; m.p. 98·0–98·5°; IR (KBr): $\nu_{as}(SO_2)$: 1299 cm^{-1}, $\nu_s(SO_2)$: 1148 cm^{-1}, $\nu_{as}(SNS)$: 956 cm^{-1}. (Found: C, 49·9; H, 4·2; N, 4·8; S, 19·9. Calc. for $C_{13}H_{12}ClNO_2S_2$ (313·84): C, 49·7; H, 3·9; N, 4·5% S, 20·4%).

S-*Methyl*-S-*phenyl*-N-(4-*methoxyphenylsulphonyl*)-*sulphilimine*. The recrystallized product was prepared by the general procedure; yield 57%; m.p. 98·5–99°; IR (KBr): $\nu_{as}(SO_2)$: 1283 cm^{-1}, $\nu_s(SO_2)$: 1138 cm^{-1}, $\nu_{as}(SNS)$: 953 cm^{-1}. (Found: C, 54·5; H, 4·8; N, 4·8; S, 20·4. Calc. for $C_{14}H_{15}NO_3S_2$ (309·41): C, 54·4; H, 4·9; N, 4·5; S, 20·7%).

Sulphuric acid. H_2SO_4 solns were prepared by dilution of pure H_2SO_4 Merck p.a. with water and titrated by standard NaOH. The H_0 values were obtained by interpolation of data published by Long and Paul[11] with the corrections above 60% of concentrations given by Jorgenson and Harter.[12]

Measurement of pK_a. pK_a data given in Tables 1 and 2 were determined by UV spectrophotometric method. The solns of sulphilimines (10^{-4}–4.10^{-4}) in H_2SO_4 of different concentrations (1–80%) were made immediately before running the spectra. The extinctions of the sulphilimine solns at wave lengths given in Tables 1 and 2 were recorded at 25° on a Beckman Model DU instrument. pK_a's were calculated from the equation

$$pK_a = H_0 + \log\frac{[SH^+]}{[S]} = H_0 + \log\frac{E - E_S}{E_{SH^+} - E}$$

by taking five different log $[SH^+]/[S]$ values from about 10% to 90% protonation. The standard deviation of pK_a's was within ±0·09 pK unit.

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