SOLVENT EFFECT IN THE REACTION OF N-SULPHONILSULPHILIMINES WITH BENZENETHIOL

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Abstract—Rate coefficients for the reactions of S,S-dimethyl-, S-methyl-S-phenyl- and S,S-diphenyl-Ntosylsulphilimine with benzenethiol in various alcohols have been determined at different temperatures. Multiparametric equations, involving specific and non-specific solute-solvent interactions, have been used to interpret quantitatively the data. The results on the solvent effect and the activation parameters indicate that the reactions proceed through the rate-determining formation of a thiol-sulphilimine adduct which occurs most likely through a cyclic transition state involving one molecule of thiol, one of sulphilimine, and one of alcohol.

N-Sulphonilsulphilimines (1) are easily reduced to the corresponding sulphides by arenethiols in methanol according to the equation (1)

In an effort to provide additional insight into this matter we have now extended these studies to a wide range of alcoholic solvents determining the reactivity

Ar¹(R)SNSO₂Ar² + 2Ar³SH
$$\rightarrow$$
 Ar¹SR + Ar³SSAr³ + Ar²SO₂NH₂ (1)
(1)
1a:R = Ar¹ = CH₃; Ar² = p-CH₃C₆H₄
1b:R = CH₃; Ar¹ = C₆H₅; Ar² = p-CH₃C₆H₄
1c:R = Ar¹ = C₆H₅; Ar² = p-CH₃C₆H₄

In an earlier kinetic study¹ on the substituent effect in Ar^1 , Ar^2 , and Ar^3 we proposed a stepwise mechanism for this reaction involving a slow reversible formation of a sulphilimine-thiol adduct (2) which rapidly collapsed to products by reaction with a



second molecule of thiol. In the same paper the question whether the formation of the adduct occurred in a single or in two step process [eq. (2)] was also discussed.

toward thiophenol of three different sulphilimines (1a-c) at various temperatures. The results of these investigations are reported herein together with a discussion of the activation parameters and of the application of multiple linear correlations involving combination of different solvent parameters in the interpretation of the solvent effect on the reaction rate.

RESULTS AND DISCUSSION

Compounds la-c react with benzenethiol in various alcohols according to eqn (1) ($Ar^3 = C_6H_5$). In all cases the kinetic runs, followed by titration of the unreacted thiol as previously described,¹ gave results fitting a second order kinetic law, first order in each reactant [eqn (3)]

$$rate = k_{obs} [Su]_{st} [PhSH]_{st}$$
(3)

$$1 + Ar^{3}SH \neq Ar^{1}(R)SNHSO_{2}Ar^{2} + Ar^{3}S^{-} \neq 2$$
(2)

However the few data collected were insufficient for discriminating between these two pathways and no definitive conclusion could be drawn in this regard. where k_{obs} is the experimental rate coefficient and [Su]_{st} and [PhSH]_{st} are the stoichiometric concentrations of the sulphilimine and of benzenethiol

	Solvent	10 ³ <u>k</u> (M ⁻¹ s ⁻¹)			
			(<u>1a</u>)	(1b)	(10)
1.	Methanol	(32.6, 0.00, 0.00, 0.586, 0.980)	225.8	63.36	2.69
2.	Ethanol	(24.3,-0.10, -0.38, 0.540, 0.826)	74.6	16.48	0.585
3.	Propan-1-ol	(20.1,-0.115,-0.67, 0.534, 0.763)	45.4	8.05	0.270
4.	Propan-2-ol	(18.3,-0.19, -1.08, 0.505, 0.695)	19.5	3.28	0.0733
5.	2-Methylpropan-1-ol	(17.7,-0.125,-1.24, - , -)	28.1	4.33	0.0983
6.	Butan-1-ol	(17.1,-0.13, -0.70, 0.503, 0.762)	37.3	6.09	0,146
7.	Bu tan-2-01	(15.8,-0.21, -1.74, - , -)	12.2	1.65	0.0251
8.	Pentan-1-ol	(13.9,-0.13, -0.71, - , -)	32.7	4.94	0.0932
9.	Benzyl alcohol	(13.1, 0.215,-0.69, 0.984, 0.430)	13.5	2.15	0.0290
10.	2-Phenylethanol	(13.0, 0.08, -0.69, - , -)	9 .0 1	1.24	0.0133
11.	2-Methylpropan-2-ol	(12.2,-0.30, -2.46, 0.534, 0.401)	4.61	0.555	0.00405 ⁰
12.	3-Phenylpropanol	(11.6, 0.02, -0.76, - , -)	5.89	-	-
13.	Heptan-1-ol	(11.0,-0.13, -0.71, - , -)	25.87	3.42	0.0487
14.	1-Phenylethanol	(8.9, 0.105, -1.80, - , -)	2.24	-	-
15.	Decan-1-ol	(7,4,-0,13,-0,71,-,-)	10.40	2.71	0.0241

Table 1. Rate coefficients for the reaction between sulphilimines (1a), (1b), and (1c) with thiophenol^a in alcohols at 30 C, with solvent parameters^b

"[Sulphilimine] = $1 \div 4.10^{-2} M$; [C₆H₅SH] = $2 \div 10.10^{-2} M$. " ϵ and σ " parameters from Ref. 5; E parameters from C. K. Hancock, E. A. Meyers and B. J. Yager, J. Am. Chem. Soc., 1961, 83, 4211; π * and α parameters from M. J. Kamlet, M. E. Jones and R. W. Taft, J. Chem. Soc. Perkin II, 1979, 342; M. J. Kamlet and R. W. Taft, *Ibid.*, 1979, 349. "Extrapolated at 30" by the relative activation parameters reported in Table 2.

respectively. Most runs were followed up to $80-90^{\circ}{}_{o}$ completion.

Values of the rate coefficients at 30° for the reactions of benzenethiol with $1a \cdot c$ in the various solvents are reported in Table 1, together with some solvent parameters. Table 2 summarizes the rate data for some reactions carried out at different temperatures with the corresponding activation parameters evaluated.

In all the solvents the reactivity order of the three sulphilimines is the same, 1a > 1b > 1c, although the effect of the solvent increases on going from 1a to 1b to 1c, as shown by the values of $k_{McOH}:k_{Bu}t_{OH}$ ratios which

at 30° are ca 49, 114, and 664 respectively. The change of the solvent seems to affect similarly the reactivity of the three sulphilimines as evidenced by the log-log plots of the rate constants of 1a and 1c against 1b which are linear with slopes 0.84 ± 0.05 (r = 0.984, s = 0.082) and 1.42 ± 0.08 (r = 0.985, s = 0.131) respectively.

In an effort to assess quantitatively our data on the solvent effect we first tentatively correlated the rate constants at 30° of **Ia** with the polarity of the solvent expressed by the Kirkwood function $f(\varepsilon)$ = (v - 1)(2v + 1).² A statistical treatment of data

Solvent S	ulphilimine	$10^{3}k (M^{-1}s^{-1})$			∆ H [≠] a_	-∆s [#] ª	
		300	40°	50°	60 °	(kcal mol ⁻¹)	$(cal mol^{-1} \cdot x^{-1})$
Methanol	(1a)	•	-	-	-	8,2 ^{<u>b</u>}	34.4 ^b
	(<u>1</u> b)	-	-	-	-	7.2 ^b	40.5 ^b
	(1e)	-	-	-	-	9.1 ^b	40.2 ^b
Ethanol	(<u>1</u> e)	0.585	0.948	1.50	-	8.5±0.5	45.21.8
Propan=1-ol (1c)		0.270	0.410	0.681	-	8.3±0.8	47.4=2.7
Butan-1-ol (1c		0,146	0.233	0.354	-	8.0±0.6	49.8±1.9
Propan-2-ol (1c)		0.0733	0.119	0.178	-	8.010.6	51•1±2•1
2-Methylpropan	-2-01 (<u>18</u>)	4.61	7.92	13.7	-	9.9±0.6	36.4-2.1
	(<u>1b</u>)	0.555	0.902	1.36	-	8,1±0,6	46.7:1.9
	(10)	-	0.00675	0.0100	0.0167	8.7±1.0 ^c	54•5±3•1 [©]

Table 2. Rate constants at various temperatures and activation parameters for some reactions of sulphilimines (1a-c) with benzenethiol in alcohols

"At 30", "From Ref. 1, "At 40 .

furnished the eqn (4) (r = 0.775, s = 0.334).

$$\log k_{\rm obs} = -10.83 + 20.32(\pm 4.90) f(\varepsilon)$$
 (4)

The positive value of regression coefficient suggests that whatever the mechanism of formation of 2 is (concerted or stepwise), the reaction is accelerated by an increase of the medium polarity. However the square of the correlation coefficient indicates that although the polar character of the solvent is important in affecting the reactivity, no more than about 60% of the solvent effect can be interpreted in terms of Kirkwood parameter. The not satisfactory fitting of the data with eqn (4) is not surprising. In fact although one term correlations with empirical parameters of solvent polarity have been sometimes found to express quantitatively the solvent effect on reactivity,³ there are many examples in which simple correlations such as eqn (4) do not hold. This fact is generally taken as an evidence of the occurrence of strong specific solute-solvent interactions. In these cases multiparametric equations have been found to describe more satisfactorily the solvent effect. The success of these correlations mainly depends on the extent to which the various solute-solvent interactions, which normally couple with one another, can be represented by separate and independent parameters.⁴ Recently Chapman et al.⁵ found that the effect of alcoholic solvents on the reaction rate between diazodiphenylmethane and carboxylic acids could be represented as a linear function of the three independent but complementary parameters $f(\varepsilon)$, σ^* and E_s (or n_y H), the Taft polar and steric substituent constants of the alkyl group of the alcohol being suitable quantitative measures of specific solventsolute interactions. Following these authors and using E_s^c instead of E_s values [as the E_s^c parameters = E_s $+0.306(n_aH-3)$ are more useful quantitative measure of the steric effect alone⁶] we tested the applicability of such a three parameter correlation to the reaction at 30° of 1a with benzenethiol. We found that the rate constants were well correlated in statistical terms with $f(\varepsilon)$, σ^* and E_s^c parameters according to the eqn (5) (r = 0.947, s = 0.184).

$$\log k_{obs} = -7.11 + 12.99(\pm 2.92) f(\varepsilon) -1.216(\pm 0.415) \sigma^* + 0.552(\pm 0.094) E_s^c$$
(5)

i. i

The success of this correlation is not inconsiderable: about 90% of the observed solvent effect can be thus explained. Moreover, the eqn (5) indicates that the rate

of the reaction between 1a and benzenethiol increases by increasing the dielectric constant of the medium and by decreasing both the electron withdrawing power[†] and the size of the alkyl group of the alcohol. If eqn (5) is changed into a form suggested by Koppel and Palm,8 the relative importance on the change of reactivity of the $f(\varepsilon)$, σ^* , and E_{ε}° terms can be better judged. For two alcohols 1 and 2 eqn (5) becomes

$$\Delta \log k = 12.99 [f(\varepsilon_1) - f(\varepsilon_2)]$$

$$-1.216(\sigma_1^* - \sigma_2^*) + 0.552(\mathbf{E}_{s_1}^c - \mathbf{E}_{s_2}^c)$$
 (6)

Using methanol as reference alcohol it results that in all cases the weight of the E^c term $[0.552(E_{3}^{c} - E_{3}^{c})]$ dominates the σ^* term $[1.216(\sigma_1^* - \sigma_2^*)]$ in determining the $\Delta \log k$ and that the contribution of E^c term increases as α -methylation in the alcohol rises. This last point is better evidenced by the values of E^c term/ σ^* term ratio which is 1.72 for the pair methanol-ethanol, 2.58 for the pair methanol-propan-2-ol, 3.72 for the pair methanol-2-methyl-propan-2-ol, 1.46 for the pair methanol-benzylic alcohol, 7.76 for the pair methanol-1-phenylethanol, 2.64 for the pair methanol-propan-1-ol and 3.76 for the pair methanolbutan-2-ol. These findings, which show the important role of the steric factor of the solvent in affecting the reactivity, appear to provide further support to the hypothesis above advanced of direct involvement of solvent molecules in the reaction mechanism.

More recently Kamlet, Taft et al.⁹ proposed a new type of three parameter equation based on the method of solvatochromic comparison for interpreting the solvent effect. Using this equation the authors were able to rationalize successfully the solvent effect on many type of chemical and spectroscopic properties and reaction rates. According to this model, the solvent effect on the reactivity parameter (XYZ) can be described through a general equation of the form

$$XYZ = XYZ_0 + s\pi^* + a\alpha + b\beta$$

where s, a, and b measure the response of XYZ to the change of the solvent polarity-polarizability (π^*) , the solvent acidity (α), and the solvent basicity (β) respectively. This equation reduces to more simple two term correlation when the effect of hydrogen bonding to the solvent or by the solvent are excluded. Unfortunately π^* , α , and β parameters are known only for a limited number of our solvents. However an attempt to apply this treatment to our data was accomplished. The most succesful correlation proved to be a two parameter combination of π^* and α , the β term being negligible [eqns (7), (8), and (9) for 1a, 1b, and 1c respectively].

$$\log k_{\rm obs} = -4.11 + 1.03(\pm 0.21)\pi^* + 2.88(\pm 0.17)\alpha$$
(7)
(r = 0.993, s = 0.079)

$$\log k_{\rm obs} = -5.46 + 1.34(\pm 0.27)\pi^* + 3.49(\pm 0.22)\alpha \tag{8}$$

$$(r = 0.992, s = 0.101)$$

$$\log k_{obs} = -8.25 + 1.67(\pm 0.29)\pi^* + 4.83(\pm 0.24)\alpha$$
(9)

$$(r = 0.995, s = 0.108)$$

Recently doubts on the real meaning of σ^* constants have been advanced by Charton,⁷ who adfirms that σ^* values of alkyl groups represent more a measure of a steric than of an electrical effect.

Assessed statistically eqns (7), (8), and (9) are considerably better correlations than eqn (5). They explain more than 98% of the observed solvent effect. The main points emerging by this approach concern (a) the positive values of s and a, (b) the a/s ratio which is larger than unity and increases going from la to lb to lc. (c) the absence of β term. Points (a) and (b) substantially confirm the results of eqns (4) and (5) on the positive role of solvent polarity in affecting the reactivity and on the direct participation of the solvent at the reaction mechanism. Moreover the positive dependence of the rate by α provides further information on the specific role played by the solvent. Along the lines of Kamlet and Taft we interpret the results of eqns (7), (8), and (9) as an evidence of the occurrence of electrophilic assistance by alcohol molecules as H-bond donors to the N atom of sulphilimine in the formation of adduct 2. Consistent with this is the increase of regression coefficient of α on going from 1a to 1b to 1c. In fact the lower the basicity of sulphilimine the larger is expected to become the requirement of acid catalysis.

Examination of Arrhenius parameters reported in Table 2 sheds further light on the probable mechanism of formation of 2. The reactivity order of the three sulphilimines in the same alcohol as well as the reaction rates of the same sulphilimine in the different solvents mainly depend on ΔS^{\neq} values, which are large and negative in all cases, the ΔH^{+} changes being small and negligible. Furthermore the increases of $-\Delta S^{*}$ on going from 1a to 1b and to 1c, more remarkable in Bu' OH than in MeOH, parallel the increases of the $k_{MeOH}:k_{Bu}t_{OH}$ ratios before reported. The more sterically hindered the sulphilimine S atom is and the more space demanding the alcohol is, the larger and more negative the activation entropy becomes. We think that such large and negative ΔS^{\pm} values cannot be in agreement with a stepwise mechanism. In this case, in fact, the ΔS^* values should be a combination of the entropic factors relative to the two stages. As an entropy increase going from reactants to the transition state may be expected for the attack of benzenethiolate ion on the protonated 1 [step ii in eqn (2)],¹⁰ the ΔS° value for the equilibrium i would be even more large and negative than the experimental ΔS^{*} values. To the best of our knowledge, no example of acid-base equilibrium reaction in alcoholic solvents with so large negative ΔS^0 values is known. So great and negative activation entropies, which suggest highly ordered transition states, have instead been generally observed for termolecular processes.11,12

In the light of all these results some useful

specific participation of the solvent in the reaction mechanism, mainly as acid catalyst. A possible transition state which in our opinion could better account for both the results on the solvent effect and activation parameters is **4**, which involves one



molecule of thiol, one of sulphilimine and one of alcohol in a cyclic arrangement. Transition states of this type have been proposed for the reaction of sulphoxides with sulphur diimides to give sulphilimines and for the base-catalysed conversion of sulphilimines to sulphoxides in MeOH.12 A similar mechanistic pathway has been also advanced for addition reactions in MeOH of HCN13 and RSH14 to the C=N bond of benzilideneanilines. The dependence of the reaction rate on the π^* and α solvent parameters could indicate that although an attack on the S=N bond of la-c occurs by an alcohol solvated thiol molecule, nevertheless it is the formation of the H-N bond which is energetically dominant. Moreover, the greater decrease in activation entropy in less polar solvents seems to confirm that a polar transition state is formed from less polar reactants. The proposed mechanism not only is compatible with large and negative ΔS^{\neq} values but also with the strong dependence of the reaction rate on E^c solvent parameters. Consistent with this mechanism are also the other kinetic results reported in previous work:¹ (i) the sign and the magnitude of ρ constants relative to the effect of the substituents in Ar¹, Ar², and Ar³ (ρ_{Ar^1} $= -0.53; \rho_{Ar^2} = -0.85; \rho_{Ar^3} = -1.83);$ (ii) the strong steric requirement of the reaction as shown by the large rate decrease with the introduction of bulky groups both in sulphilimine and in thiophenol; (iii) the fact that the reaction (1) is completely inhibited in solvents such as benzene, dioxan, and chloroform which have no H- bond donor character.

Final support for a concerted addition of thiol to sulphilimine is furnished by the results reported by Oae *et al.*¹⁵ for the reaction of S-alkyl-S-aryl-N-p-tosylsulphilimines with thiophenolate ion in MeOH [eqn (10)]

indications on the reaction mechanism seem to emerge. Actually, activation parameters seem to be more in agreement with a concerted than with a stepwise addition of thiol to sulphilimine while the data on the solvent effect seem to be consistent with a

which affords quantitatively alkyl phenyl sulphide, diaryldisulphide and tosylamide through a mechanism involving an aliphatic nucleophilic attack of thiolate on the C atom adjacent to the sulphur of sulphilimine. It seems evident that if the formation of adduct 2 occurred through a stepwise mechanism as in eqn (2), the immino sulphonium cation 3 once formed in the step i should undergo at least a competitive attack of PhS⁻ on carbon and sulphur with formation in the

tAs the imide RSNHTs is surely a better leaving group than its conjugate base in an aliphatic substitution, the attack on C atom should be favoured.

case of the reaction on 1a of methyl phenyl sulphide besides the dimethyl sulphide, the diphenyldisulphide and the tosylamide. Therefore the absence of the methyl phenyl sulphide among the products of the reaction on 1a seems to be another argument in favour of a concerted mechanism.

EXPERIMENTAL

Materials. Solvents were purified according to the literature procedures.⁵ Sulphilimines 1a-c were prepared by known methods.¹⁶

Product analysis. The reaction products were isolated in separate experiments carried out under conditions identical to those used in the kinetic runs and identified by tlc, glc¹⁵ and mixed m.p. with authentic samples.

Kinetic procedure. Reactions were followed as previously reported¹ by titration of the unreacted benzenethiol. From the analytical data and the stoichiometric equation [eqn (1)] the concentration of the reagents at any time was calculated. The second-order rate constants were evaluated graphically.¹⁷ Each value of the rate constants reported in the Tables is the average of three or more independent runs. The rate constants at various temperatures obeyed the Arrhenius equation and the activation parameters were evaluated by standard methods.¹⁸

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