Organic Chemistry

The Solvent Effect in the Reaction of N-Sulphonil-sulphilimines with Arenethiols in Alcohol

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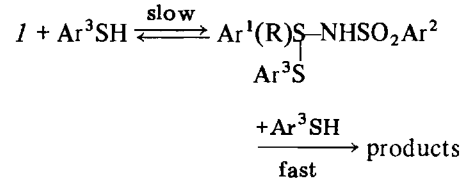
A detailed study of the solvent effect and of activation parameters indicates that most likely the mechanism of sulphilimine reduction by arenethiols in alcohol [1] thus

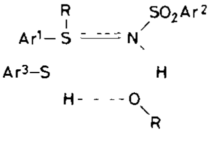
$$Ar^1(R)SNSO_2Ar^2 + 2\ Ar^3SH \rightarrow Ar^1SR + Ar^3SSAr^3 + Ar^2SO_2NH_2 \qquad (1)$$

is as follows



$$1 + Ar^3SH \underset{}{\overset{\text{slow}}{\rightleftharpoons}} Ar^1(R)\underset{Ar^3S}{S}\text{–}NHSO_2Ar^2 \xrightarrow[\text{fast}]{+Ar^3SH} \text{products} \qquad (2)$$

in which the formation of *2* occurs through a cyclic transition state *3* involving the participation of one molecule of sulphilimine, one of thiol and one of alcohol



(3)

A quantitative analysis of the solvent effect through multiparametric equations evidences the relative weight of the specific and non specific solute–solvent interactions For $Ar^1 = R = CH_3$, $Ar2 = p\text{-}CH_3C_6H_4$, $Ar^3 = C_6H_5$ the second order rate constants satisfy the following equations

$$\log k = -7\ 11 + 12\ 99(\pm 2\ 92)f(\epsilon) - 1\ 216(\pm 0\ 415)\sigma^* + 0\ 552(\pm 0\ 094)E_s^c$$

($r = 0\ 947, s = 0\ 184$) (Chapman treatment [2])

$$\log k = -4\ 11 + 1\ 03(\pm 0\ 21)\pi^* + 2\ 88(\pm 0\ 17)\alpha$$

($r = 0\ 993, s = 0\ 079$) (Kamlet and Taft treatment [3])

References

1 G Guanti, G Garbarino, C Dell'Erba and G Leandri, *Gazzetta, 105,* 849 (1975)
2 N B Chapman, M R J Dack and J Shorter, *J Chem Soc (B),* 834 (1971)
3 M J Kamlet and R W Taft, *J Chem Soc Perkin II,* 337, 349 (1979),
M J Kamlet, M E Jones and R W Taft, *ibid*, 342 (1979)

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1 1 Molecular Adducts between I_2 and Tio- (or Seleno-) amido Group Contained in Some Heterocyclic Rings

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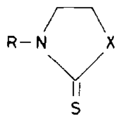
The donor properties of Y (= S or Se) in RN·CY·X group are affected by the nature of X This fact has been pointed out by the stability constants (K) of the 1 1 molecular adducts between I_2 and the above group contained in the following pentaatomic rings [1, 2]



R	X	R	X
H	CH_2	H	NMe
H	O	H	NEt
H	S	Me	S
H	NH	Me	NMe
		Et	NEt