Organic Chemistry

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

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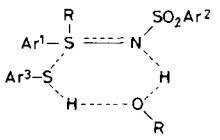
A detailed study of the solvent effect and of activation parameters indicates that most likely the mechanism of sulphilimine reduction by arenethiols in alcohol [1] thus:

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

is as follows:

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

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).

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

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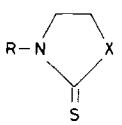
The donor properties of Y (= S or Se) in RN·CY·X group are affected by the nature of X. This fact has been pointed out by the stability constants (K) of the 1:1 molecular adducts between I_2 and the above group contained in the following pentaatomic rings [1, 2]:

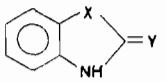


R	X	R	X
H	CH_2	H	NMe
H	O	H	NEt
H	S	Me	S
H	NH	Me	NMe
		Et	NEt

This study showed that K depends on the solvent, R and X. For the same solvent and R, K's increase in the order O < S < CH_2 < imidazolidines (NH, NMe and NEt).

On passing from thio- to seleno-ketonic compounds (Y = Se) the K's strongly increase, keeping the same dependence on the solvent and R. For the very high values of K, the simultaneous calculation of ϵ (molar extinction coefficient of the adduct) and K has presented some problems. In fact all the methods, based on a linear least square method, fail since they give not consistent values of K. *Viceversa,* good results have been obtained by employing the no-linear least square procedures of Gauss [3] and Conrow [4], working on several solutions within a large range of the saturation fraction [5].

This kind of investigation has been now extended to the following molecules



X = O, S, NH
Y = S, Se

in order to evidentiate the changes produced by the benzene ring on the donor properties of Y.

References

1 F. A. Devillanova and G. Verani, *Tetrahedron, 35,* 511 (1978).
2 F. A. Devillanova and G. Verani, *J. Heterocyclic Chem., 16,* 945 (1979).
3 D. R. Rosseinsky and H. Kellawi, *J. Chem. Soc. A,* 1207 (1969).
4 K. Conrow, G. D. Johnson and R. E. Bowen, *J. Am. Chem. Soc., 86,* 1025 (1964).
5 G. Carta and G. Crisponi, private communication.

Electronic, Steric and Lipophilicity Requirements in the Oxidation of Dialkylarylamines by Horseradish Peroxidase

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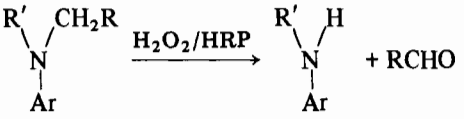
Horseradish peroxidase (HRP) catalyzes the oxidation of a wide variety of organic compounds by hydrogen peroxide. The mechanism has been established and described by the following scheme:

$$HRP + H_2O_2 \rightleftarrows HRP{-}H_2O_2 \rightarrow E_1$$

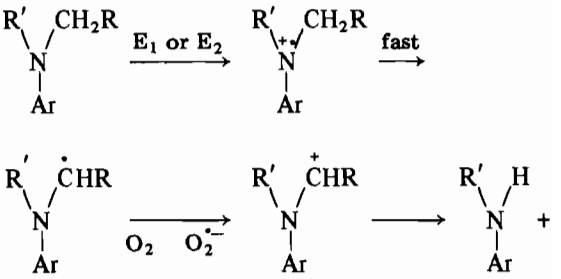
$$E_1 + AH_2 \rightleftarrows E_1{-}AH_2 \rightarrow E_2 + AH^{\bullet}$$

$$E_2 + AH_2 \rightleftarrows E_2{-}AH_2 \rightarrow HRP + AH^{\bullet}$$

where E_1 and E_2 are oxidized forms of the enzyme at respectively two and one level of oxidation. In previous work we have shown that HRP catalyzes the oxidation of aromatic tertiary amines with hydrogen peroxide yielding a secondary amine and an aldehyde according the reaction



In this reaction oxygen is consumed. From stoicheiometrical experiments the following mechanism has been proposed:



Since the hydrogen peroxide–peroxidase system is often regarded as a simple model for more complex biological oxidative systems, we have studied the structure requirements in the oxidation of some dialkylarylamines with this system.

A kinetic investigation was performed on a series of fifteen N,N-dimethyl (*1–8*) and diethylanilines (*9–15*). Within the experimental range of concentrations initial rates were linearly dependent on initial substrate concentrations. The apparent first order constants were calculated. Diethylanilines react on the average 2.6 times faster than dimethylderivatives. This parallelism reduces the possibility of dealing with random points distribution. In spite of this, statistical treatment of data by single or multiple regression does not show any linear expression of reactivity as a function of Hammett's σ, Hansch's π lipophilicity and MR steric parameters. Different rate determining steps may be supposed within the substrates series. However some empirical observations can be made. Reactivity is lowered by hydrophobic and electron withdrawing substituents and exalted by hydrophilic and electron donor substituents. Bulkiness of substrate has no peculiar importance. These results are in analogy with other data