

Linear Free Energy Relationship in Naphthalene System: Kinetics of Oxidation of 6-Substituted 2-Naphthyl Methyl Sulphides with Peroxoanions

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Oxidation of some 6-substituted 2-naphthyl methyl sulphides by peroxodisulphate and peroxodiphosphate ions in acetic acid-water mixture follows second order kinetics, first order each in the substrate and the oxidant. The rate data show good correlations with σ_p^+/σ_p^- constants rather than with σ_p or σ_p^+ constants. Multiple regression analyses of the rate data employing the dual substituent parameter equation show that the transmission of both inductive and resonance effects is less in the 6,2-series relative to the 4,1-series.

We have recently reported¹ results of correlation studies on the kinetics of peroxodisulphate (PS) and peroxodiphosphate (PP) oxidations of several 4-substituted 1-naphthyl methyl sulphides (hereafter referred to as 4,1-series). The PS and PP oxidations of 6-substituted 2-naphthyl methyl sulphides (hereafter referred to as 6,2-series) have now been studied with a view to finding the applicability of the Hammett equation to the 6,2-series. The results have been compared with those of the 4,1-series¹.

The oxidations, PS and PP were used after crystallisation¹. Methyl 2-naphthyl sulphide, 6-methylthio-2-acetonaphthone, 6-ethyl-2-naphthyl methyl sulphide and 6-acetamido-2-naphthyl methyl sulphide were prepared by literature methods^{1,2}. 6-Methyl-2-naphthyl methyl sulphide was prepared by the reduction of the corresponding sulphonyl chloride³ followed by methylation. 6-Iodo-2-naphthyl methyl sulphide was obtained from 6-amino-2-naphthyl methyl sulphide². The purity of all the sulphides was checked by elemental analyses.

The kinetics were followed iodometrically¹ under pseudo-first order conditions in 70% acetic acid-30% water (v/v) at constant $[H^+]$ and ionic strength at 30°C. However, due to solubility difficulties the substituent effects of all the sulphides in 6,2-series were studied in 85% acetic acid-15% water (v/v). The pseudo-first order rate constants were evaluated by the least-squares method.

The PS and PP oxidations of the methyl 2-naphthyl sulphide follow second-order kinetics, first order in each reactant as shown by (i) the linear plots of

$\log[\text{oxidant}]$ versus time and (ii) the linear plots of pseudo-first order rate constants versus [sulphide] passing through the origin (curves not included). The PS oxidation of the sulphide is not significantly influenced by $[H^+]$ while the PP oxidation shows first order dependence on $[H^+]$ and the linear plot of k_2 versus $[H^+]$ passes through the origin ($k_2 = k_1/[H^+]$). The product in both the oxidations was found to be methyl 2-naphthyl sulfoxide by TLC and the stoichiometry of the oxidation reaction was 1:1 for both PS and PP oxidations (for details see ref. 1).

The rate data show that electron-donating substituents enhance the rate while electron-withdrawing ones retard it (Table 1). These results suggest the rate-limiting formation of sulphonium ions (formed by the attack of $S_2O_8^{2-}$ in PS and $H_3P_2O_8^-$ in PP oxidations) followed by their conversion into the sulfoxide in a fast step^{1,4-6}.

The rate data of the 6,2-series appear to correlate well with σ_p^+/σ_p^- constants rather than with σ_p or σ_p^+ constants (Table 2). The simultaneous incorporation of σ_p^+ and σ_p^- constants is justified by the $\pm M$ effect of the

Table 1—Second Order Rate Constants for Oxidation of 6-Substituted 2-Naphthyl Methyl Sulphides with PS and PP

[Sulphide] $\gg$ [oxidant]; solvent = 85% CH_3COOH - 15% H_2O (v/v); temp. = 30°C
 $10^3 k_2$ ($dm^3 mol^{-1} s^{-1}$)

Substituent	PS	PP
	($I = 0.02 mol dm^{-3}$)	($I = 0.20 mol dm^{-3}$)
NHAc	14.4 ± 0.32	21.7 ± 0.58
Me	13.3 ± 1.2	19.0 ± 1.5
Et	12.7 ± 0.17	18.4 ± 0.47
H	9.54 ± 0.30	14.2 ± 0.42
I	9.67 ± 0.78	12.3 ± 0.49
COMe	6.32 ± 0.50	7.06 ± 0.46

*The error quoted in rate constants is in 95% confidence level of the student's t-test

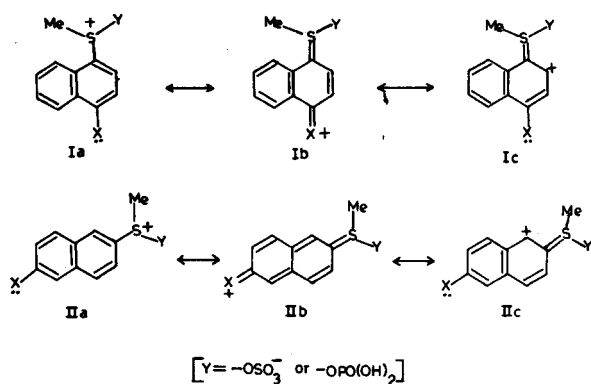
Table 2—Applicability of Hammett Equation to Rate Data in 6,2-Series in PS and PP Oxidations

Oxidant	Substituent constant	ρ	Corr. coeff.	St. dev.	n
			(r)		
PS	σ_p	-0.438	0.873	0.07	6
	σ_p^+	-0.332	0.976	0.03	6
	σ_p^+/σ_p^-	-0.264	0.987	0.02	6
PP	σ_p	-0.660	0.919	0.08	6
	σ_p^+	-0.446	0.977	0.04	6
	σ_p^+/σ_p^-	-0.358	0.996	0.02	6

Table 3—Correlations of Rate Data of 4,1-Series^a and 6,2-Series Using Dual Substituent Parameter Equation

Series	Oxidant	Substituent constant	ρ_I	ρ_R	Corr. coeff. (R)	S _E ^b	n
6, 2	PS	$\sigma_I, \sigma_R^+/\sigma_R^-$	-0.302	-0.264	0.987	0.03	6 ^c
	PP	$\sigma_I, \sigma_R^+/\sigma_R^-$	-0.453	-0.347	0.999	0.01	6 ^d
4, 1	PS	$\sigma_I, \sigma_R^+/\sigma_R^-$	-0.818	-0.767	0.993	0.04	8 ^d
	PP	$\sigma_I, \sigma_R^+/\sigma_R^-$	-0.781	-0.675	0.997	0.02	8 ^d

Rate data of the 4,1-series (substituents: MeO, Me, Et, H, F, Cl, Br and COMe) were taken from ref. 1; ^bstandard error of the estimate; ^ccorrelation justified by >99.5% confidence level of F-test and >98% in the t-test; and ^dcorrelation justified by >99.9% confidence levels of the F- and t-tests



sulphur atom, which depends on the substituent in the aryl moiety⁵⁻⁷.

In order to quantitatively separate the inductive and resonance contributions to the substituent effects the rate data of the 4,1- and 6,2-series have been analysed using the dual substituent parameter (DSP) equation (1)

$$\log k_2 = \rho_I \sigma_I + \rho_R \sigma_R + h \quad \dots (1)$$

The substituent parameters, σ_I , σ_R^0 , σ_R^+ , σ_R^- and σ_R^- were taken from the compilation of Exner⁸. The results of the best fits as judged by the confidence levels of F- and t-tests presented in Table 3 reveal that in both oxidations, the rate data¹ of the 4,1-series give good correlations with σ_I , σ_R^+/σ_R^- constants while those of the 6,2-series correlate well with σ_I , σ_R^+/σ_R^- constants. The only substituent (acetyl) warranting the use of σ_R^- in the 6,2-series suffers steric inhibition of resonance¹ when present in the 4-position of the naphthyl ring and hence

σ_R is employed for acetyl group in the 4,1-series. The susceptibility parameters, ρ_I and ρ_R of the 6,2-series are less than those of the 4,1-series (Table 3) indicating a diminution in the transmission of both inductive and resonance effects in the 6,2-series.

The low ρ_I values of the 6,2-series are due to the fact that the substituents in this series are separated by several bonds from the reaction site relative to the 4,1-series. The lower ρ_R values in the 6,2-series as compared to 4,1-series are explained as follows: The intermediates, I in the 4,1-series and II in the 6,2-series formed in the rate-limiting steps would be stabilized by the +M effect of the substituents (see structures Ib and IIb). Further these canonical forms contribute more to their respective resonance hybrids. However, IIb is less stable than Ib, since the aromaticity of both the rings are disturbed in IIb leading to instability and consequently lowering of ρ_R values.

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