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Kinetics and Mechanism of the Oxidation of Organic Sulfides by *N*-Bromobenzamide

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Kinetics of oxidation of 34 organic sulfides by *N*-bromobenzamide (NBB), to yield the corresponding sulfoxides, have been studied. The reaction is first-order with respect to the sulfide, NBB, and hydrogen ions. There is no effect of added benzamide. Protonated NBB has been postulated as the reactive oxidizing species. Reactivity of the sulfides toward NBB was subjected to correlation analysis by using multiparametric equations. The polar reaction constants are negative. Steric effects play a minor inhibitory role. A mechanism involving formation of a halogenosulfonium cation, in the rate-determining step, has been proposed.

Kinetics and mechanism of the oxidation of organic sulfides have received considerable attention in recent years.[1-11] The mechanism depends largely on the nature of the oxidant. In the oxidation of sulfides by *N*-bromoacetamide (NBA),[3] studied in the presence of Hg(II), it has been suggested that both NBA and the sulfide form complexes with Hg(II) and these complexes participate in the rate-determining step. Oxidations by *N*-bromobenzamide (NBB)[12] do not require the presence of Hg(II) as a bromine scavanger. In this paper, kinetics of oxidation of 34 organic sulfides by NBB in acid solutions are reported. Attempts have been made to correlate rate and structure.

The oxidation of organic sulfides by NBB results in the formation of corresponding sulfoxides (eq 1).

$$\mathrm{RSR' + PhCONHBr + H_2O \rightarrow RS(O)R' + PhCONH_2 + HBr} \quad (1)$$

The oxidation of sulfides by NBB is first-order with respect to NBB. The variation in the concentration of the sulfide indicates that the reaction is first-order with respect to the sulfide also. The reaction rate increases linearly with an increase in the hydrogen ion concentration (Table I).

Added benzamide has no effect on the rate of reaction. The oxidation of methyl phenyl sulfide was studied in solvents containing different proportions of acetic acid and water. The rate of reaction is decreased as the amount of water in the solvent is increased. The rates of oxidation of a number of ortho-, meta-, and para-substituted phenyl methyl sulfides, alkyl phenyl sulfides, dialkyl sulfides, and diphenyl sulfide were determined at different temperatures, and the activation parameters were calculated (see the supplementary material).

Table I. Rate Constants of the Oxidation of Methyl Phenyl Sulfide by NBB at 298 K

[MeSPh], M	10^3[NBB], M	[H^+], M	10^5k_1, s^{-1}
0.5	2.5	1.0	6.30
0.5	5.0	1.0	6.25
0.5	7.5	1.0	6.32
0.5	10.0	1.0	6.18
0.5	15.0	1.0	6.20
0.2	5.0	1.0	2.57
0.8	5.0	1.0	9.87
1.0	5.0	1.0	12.5
1.4	5.0	1.0	17.3
1.7	5.0	1.0	21.5
2.0	5.0	1.0	25.2
1.0	5.0	0.3	3.69
1.0	5.0	0.6	7.70
1.0	5.0	1.2	15.0
1.0	5.0	1.5	19.0
1.0	5.0	1.8	22.2
1.0	5.0	2.1	26.4

The linear increase in the reaction rate with acidity suggests a protonation of NBB to give a stronger oxidant and electrophile (eq 2).

$$\mathrm{PhCONHBr + H_3O^+ \rightleftarrows (PhCONH_2Br)^+ + H_2O} \quad (2)$$

The observed solvent effect can be attributed to the increase in the protonating power of the solution with an increase in the amount of acetic acid[13] and/or to the decreased polarity of the transition state as compared to the reactant state. This is also in accord with the postulation of a protonation of a neutral species in the preequilibrium.

The oxidation rates of meta- and para-substituted phenyl methyl sulfides failed to show satisfactory correlation with any single substituent-parameter equation. The rates of the meta and para compounds were, therefore, subjected to analysis in terms of Taft's[14] and Swain's[15] dual substituent-parameter (DSP) equations. The rates of the para-substituted sulfides show an excellent correlation with σ_I and σ_R^+ values (Table II). We have used standard deviation (SD), coefficient of multiple correlation (R), and the parameter f as the measures of goodness of fit. f has been defined[16] as SD/root mean square of data points (here $\log k/k_0$). Comparison showed that f is smaller for the σ_R^+ scale than for the other scales by factors of ca. 5-12. Thus it is apparent that the rates of the oxidation of

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Table II. Correlation of the Rates of Oxidation of Para- and Meta-Substituted Phenyl Methyl Sulfides by NBB at 298 K[a]

subst constants	ρ_I	ρ_R	R	SD	f
		Para Substituted			
σ_I, σ_R°	-1.56	-3.18	0.9319	0.39	0.16
σ_I, σ_R^{BA}	-1.41	-2.46	0.9813	0.21	0.09
σ_I, σ_R^-	-1.49	-1.80	0.8097	0.63	0.25
σ_I, σ_R^+	-1.15	-1.50	0.9990	0.05	0.02
Swain et al.[b]	-0.30	-0.82	0.9801	0.25	0.11
		Meta Substituted			
σ_I, σ_R°	-1.49	-0.95	0.9974	0.04	0.05
σ_I, σ_R^{BA}	-1.62	-0.71	0.9680	0.15	0.19
σ_I, σ_R^-	-1.63	-1.13	0.9906	0.08	0.10
σ_I, σ_R^+	-1.63	-0.37	0.9513	0.18	0.23
Swain et al.[b]	-0.91	-0.28	0.9690	0.14	0.19

[a] SD = standard deviation, R = coefficient of multiple correlation, f = SD/(root mean square of $\log k/k_0$); σ_I and σ_R are from ref 14. [b] Field and resonance constants are from ref 15.

para-substituted phenyl methyl sulfides by NBB correlate best with σ_I and σ_R^+.

The rates of the oxidation of the meta compounds show excellent correlation with σ_I and σ_R°, although the discriminating factor for the precision of fit with the other σ scales or with Swain's equation is not as sharp as in the case of para-substituted compounds. In fact the correlation with σ_R^- meets the requirements for a satisfactory fit ($f < 0.1$). This agrees with the observation of Ehrenson, Brownlee, and Taft[16] that the correlation of meta-substituted compounds is generally best with σ_R° and meta-substituted compounds are less discriminating.

The reaction constants and statistical data were determined at different temperatures (see the supplementary material). The value of λ^p (1.26–1.40) showed that the oxidation of the para-substituted sulfides is more susceptible to the resonance effect than to the field effect. In the oxidation of the meta-compounds, however, the value of λ^m is in the range of 0.59–0.71, indicating the greater importance of the field effect.

In none of the earlier reports on the oxidation of sulfides have DSP equations been used for correlating the effect of structure on reactivity. In oxidations by reagents which involved a direct oxygen transfer via an electrophilic attack on the sulfide sulfur, the reaction constants are negative but are of relatively small magnitude, e.g. hydrogen peroxide (-1.13),[17] periodate (-1.40),[9] permanganate (-1.52),[10] and peroxydisulfate (-0.56).[4] The reactions involving formation of halogenosulfonium cations, on the other hand, exhibit large negative reaction constants (cf. -4.25, -3.2, and -2.37 for the oxidation of sulfides by chloramine-T,[1a] bromine[2b] and NBA,[3] respectively). In the present study, the total effect of the meta and para substituents have been dissected into contributions by inductive and resonance effects. The reaction constants are large and negative. Thus the formation of a strongly electron deficient sulfur center in the transition state is indicated.

The rates of the oxidation of ortho-substituted phenyl methyl sulfides failed to yield any significant correlation with either Taft's polar or steric substituent constants.[18] The rates were, therefore, analyzed by Charton's method.[19] The rates were analyzed using eqs 3 and 4, where σ_I, σ_R, and V are field, resonance, and steric substituent constants; the values used were those compiled by Aslam et al.[20] The results of correlation in terms of eq 3 are given in eq 5, where n is the number of data points. In the multiple linear regression using eq 3, the correlation coefficient is poor and the standard deviation is high. This showed that only electrical effects are not sufficient to account for the observed ortho effect in the oxidation of sulfides by NBB. Here ψ is Exner's statistical parameter.[21] According to Exner,[21] this value of ψ also means that the correlation is poor.

$$\log k_{\text{ortho}} = \alpha\sigma_I + \beta\sigma_R + h \tag{3}$$

$$\log k_{\text{ortho}} = \alpha\sigma_I + \beta\sigma_R + \phi V + h \tag{4}$$

$$\log k = -2.61\sigma_I - 2.22\sigma_R - 4.35 \tag{5}$$

$$R = 0.8741;\ \text{SD} = 0.52;\ \psi = 0.48;\ n = 10$$

Correlation in terms of eq 4 was performed assuming both orthogonal and planar conformations for NO_2 and COOMe groups. The correlation was better with an orthogonal conformation of both the groups. The results (eq 6) showed that the correlation with eq 4 is poor.

$$\log k = -1.89\sigma_I - 2.47\sigma_R - 1.39V - 3.74 \tag{6}$$

$$R = 0.8901;\ \text{SD} = 0.47;\ \psi = 0.42;\ n = 10$$

Since the rates of the oxidation of meta- and para-substituted sulfides showed excellent correlation in Taft's DSP equation[14] with σ_R° and σ_R^+, respectively, the rates of the ortho-substituted sulfides were correlated in triparametric equations using Taft's σ_I and $\sigma_R^\circ/\sigma_R^+$, and Charton's steric parameters. Excellent correlation were obtained with Taft's σ_I and σ_R^+ and Charton's V values (eq 7). The behavior of NO_2 and COOMe groups is consistent with their orthogonal conformations.

$$\log k = -1.64\sigma_I - 1.28\sigma_R^+ - 1.04V - 3.84 \tag{7}$$

$$R = 0.9988;\ \text{SD} = 0.06;\ \psi = 0.06;\ n = 10$$

To test the significance of the three substituent constants, multiple linear regressions were carried out with Taft's σ_I and σ_R^+, Taft's σ_I and V, and σ_R^+ and V. The absence of significant correlations (see the supplementary material) showed that all the three substituent constants are significant.

There is no significant collinearity between Taft's σ_I and V, σ_R^+ and V, and Taft's σ_I and σ_R^+ (r = 0.3519, 0.0268, and 0.3592, respectively).

Analysis of the rates of oxidation of alkyl phenyl sulfides separately with Taft's σ^* and E_s values did not yield satisfactory correlation. The rates were, therefore, analyzed by the Pavelich–Taft[22] DSP equation (8). The re-

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sults of correlation is given in eq 9.

$$\log k = \rho^*\sigma^* + \delta E_s + h \qquad (8)$$

$$\log k = -2.34\sigma^* + 0.94E_s - 3.90 \qquad (9)$$

$$R = 0.9999;\ \mathrm{SD} = 0.01;\ \psi = 0.02;\ n = 5$$

The number of compounds (five) is rather small for an analysis by a biparametric equation, but the correlations are excellent and the results can be used in a qualitative way. The negative polar reaction constant confirms that the electron-donating power of the alkyl groups enhances the rate. The steric effect plays a minor inhibitory role. There is no significant collinearity between σ^* and E_s of the five substituents ($r = 0.6231$).

The experimental results can be accounted for in terms of a rate-determining electrophilic attack of a protonated NBB molecule on the sulfide to yield a halogenosulfonium ion. The large negative reaction constants and correlation of the rates of the ortho- and para-substituted compounds with σ^+ values indicated that, in the transition state, there is a strong resonance interaction of the substituents in the aromatic ring with a developing positive charge at the sulfur center. There is a considerable steric interaction also between the ortho substituents and the reaction center in the transition state. Thus one can visualize the following mechanism for the reaction.

$$\mathrm{PhCONHBr} + \mathrm{H_3O^+} \rightleftharpoons (\mathrm{PhCONH_2Br})^+ + \mathrm{H_2O} \qquad (2)$$

$$\mathrm{R_2S} + \mathrm{Br^+NH_2COPh} \xrightarrow{\text{slow}} \mathrm{R_2S^+Br} + \mathrm{PhCONH_2} \qquad (10)$$

$$\mathrm{R_2S^+Br} + \mathrm{H_2O} \xrightarrow{\text{fast}} \rightarrow \mathrm{R_2S^+OH} + \mathrm{HBr} \qquad (11)$$

$$\mathrm{R_2S^+OH} \xrightarrow{\text{fast}} \mathrm{R_2S{=}O} + \mathrm{H^+} \qquad (12)$$

Experimental Section

Materials. The sulfides were either commercial products or prepared by known methods[9,23-28] and were purified by distillation under reduced pressure or crystallization. Their purity was checked by comparing their boiling or melting points with the literature values. NBB was prepared by the reported method.[29] Acetic acid was refluxed over chromic oxide for 6 h and then fractionally distilled.

Product Analysis. Methyl phenyl sulfide (0.005 mol) and NBB (0.005 mol) were dissolved in 1:1 (v/v) acetic acid–water (40 mL) in the presence of perchloric acid (0.002 mol), and the mixture was allowed to stand for 24 h. Most of the solvent was removed under reduced pressure. The residue was diluted with water and extracted with chloroform (3 × 50 mL). The chloroform layer was dried over anhydrous magnesium sulfate, the solvent was removed by evaporation, and the residue was analysed by IR spectroscopy. The spectrum was identical with that of an authentic sample of MeSOPh.

Kinetic Measurements. Kinetic measurements were carried out under pseudo-first-order conditions by keeping an excess (15× or greater) of the substrate over NBB. The reactions were carried out at constant temperature (±0.05 K). The solvent was 1:1 (v/v) acetic acid–water, unless stated otherwise. Preliminary experiments showed that the reaction is not sensitive to ionic strength (0.05–2.5 M); hence no attempt was made to keep the ionic strength constant. The reactions were followed iodometrically for up to 80% of the extent of reaction. The observed rate constant, k_1, was determined from the linear (r = 0.990–0.999) plots of log [NBB] against time. The specific rate constant, k, was obtained from the relation: $k = k_1/[\text{sulfide}][\mathrm{H^+}]$. Duplicate kinetic runs showed that the rates were reproducible to within ±3%.

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Supplementary Material Available: Tables of the effect of benzamide and solvent composition on rate, rate constants at different temperatures, activation parameters, reaction constants and statistical parameters at different temperatures, details of correlation analysis with various parameters (6 pages). Ordering information is given on any current masthead page.

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