Kinetics and Mechanism of the Oxidation of Organic Sulfides by Pyridinium Bromochromate

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The oxidation of organic sulfides by pyridinium bromochromate proceeds through an acyclic sulfurane transition state.

Pyridinium bromochromate (PBC) is a mild oxidizing agent.[3] In the oxidation of organic sulfides, PCC[10] exhibits Michaelis–Menten type kinetics with respect to the reductant whereas a first-order dependence is obtained in the oxidation by PFC.[11] There do not appear to be any reports on the kinetics of the oxidation of sulfides by PBC. We now report the kinetics of the oxidation of 34 organic sulfides by PBC. A probable mechanism is proposed.

PBC was prepared by a reported method.[3] The reactions were studied under pseudo-first-order conditions by using an excess ($15 \times$ or greater) of the sulfide. *N,N*-Dimethylformamide (DMF) was used a solvent unless otherwise stated. The reactions were followed by monitoring the decrease in the concentration of PBC at 356 nm for up to 80% of the reaction duration. Pseudo-first-order rate constants, k_{obs}, were evaluated from linear plots ($r > 0.990$) of log[PBC] against time.

The oxidation of organic sulfides by PBC resulted in the formation of the corresponding sulfoxides. Product analysis indicated the following overall reaction [eqn. (1)].

$$R-S-R' + CrO_2BrOpyH \longrightarrow \underset{\underset{O}{\overset{\|}{}}}{R-S}-R' + CrOBrOpyH \quad (1)$$

The reactions are first-order with respect to PBC and the sulfide. The oxidation of methyl phenyl sulfide, in an atmosphere of nitrogen, failed to induce the polymerization of acrylonitrile. The reaction is catalysed by hydrogen ions, the dependence on which has the form: $k_{obs} = c + d[H^+]$. This suggests protonation of PBC in a pre-equilibrium with both PBC and PBCH$^+$, PBCH$^+$ being the reactive oxidizing species.

The oxidation of MeSPh was studied in 19 different organic solvents. The kinetics were similar in all the solvents. However, the rate constants for the oxidation in 18 of the solvents (CS$_2$ was not considered, as the complete range of solvent parameters was not available) did not show a satisfactory correlation in terms of the linear solvation energy relationship of Kamlet *et al.*[21]

The solvent effect data exhibited excellent correlation in terms of Swain's equation[23] of the cation- and anion-solvating abilities of the solvents [eqn. (8)], with the cation-solvating power being slightly more important [eqn. (9)].

$$\log k_2 = aA - bB + C \quad (8)$$

$$log \, k_2 = 1.72(\pm 0.06)A + 1.99(\pm 0.05)B - 6.86 \quad (9)$$

$$R^2 = 0.9934; \qquad sd = 0.05; \qquad n = 19$$

The solvent polarity, represented by $(A + B)$, also accounted for *ca.* 99% of the data. However, the correlations individually with A and B were poor ($r^2 = 0.2179$ and 0.6842 respectively).

The rates of oxidation of a number of *ortho-*, *meta-* and *para*-substituted methyl phenyl sulfides, alkyl phenyl sulfides, dialkyl sulfides and diphenyl sulfides were determined at different temperatures and the activation parameters were calculated.

The rates of the oxidation of *meta-* and *para*-substituted aryl methyl sulfides were correlated in terms of Charton's[27] triparametric LDR equation [eqn. (13)].

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + h \quad (13)$$

Here, σ_1 is a localized effect parameter, σ_d is the intrinsic delocalized electrical effect parameter when active site electronic demand is minimal and σ_e represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by eqn. (13)

$$\sigma_D = \eta\sigma_e + \sigma_d \quad (14)$$

where η represents the electronic demand of the reaction site which is given by $\eta = R/D$, and σ_D represents the delocalized electrical parameter of the diparametric LD equation.

For *ortho*-substituted compounds, the LDR equation was modified to the LDRS equation [eqn. (15)],[27] where V is the well known Charton's steric parameter based on van der Waals radii.[28]

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + SV + h \quad (15)$$

The rates of oxidation of the *ortho-*, *meta-* and *para*-substituted sulfides show excellent correlations with their structures in terms of the LDR/LDRS equations with all the three regression coefficients, L, D and R, being negative. This indicates an electron-deficient sulfur centre in the transition state of the rate-determining step. The positive value of η adds a negative increment to σ_d [eqn. (14)], thereby increasing the electron-donating power of the substituent and its capacity to stabilize a cationic species. The negative value of S indicates that the reaction is sterically hindered by the *ortho*-substituent. This may be due to steric hindrance to the approach of the oxidizing species by the *ortho*-substituent.

The oxidation rates of the alkyl phenyl sulfides showed excellent correlations in terms of the Pavelich–Taft[37] dual substituent-parameter (DSP) equation [eqn. (18)]. The negative polar reaction constant confirms that the electron-donating power of the alkyl group enhances the reaction rate. The steric effect plays a minor inhibitory role.

$$\log k_2 = \rho^*\sigma^* + \delta E_s + \log k_0 \quad (18)$$

The experimental results can be accounted for in terms of the rate-determining electrophilic oxygen transfer from PBC to the sulfide [eqn. (20)]. The nucleophilic attack of a sulfide-sulfur on a PCB-oxygen may be viewed as an S_N2 process. Low magnitudes of the polar reaction constants support a transition state depicted in eqn. (20) rather than a sulfonium ion as shown in eqn. (21). The observed solvent effect also supports an S_N2-like transition state.

$$R-S-R' \; + \; CrO_2BrO^-pyH^+ \; \longrightarrow \quad \overset{R}{\underset{R'}{\diagdown}} S^+\!-O\!-\!\overset{O^-pyH^+}{\underset{O^-}{\overset{}{Cr}}}\!Br \qquad (21)$$

The oxidation of sulfides by PBC may involve a cyclic intermediate as has been suggested in many reactions of Cr^{VI}.[40] The cyclic transition state will be highly strained in view of the apical position of a lone pair of electrons or an alkyl group [eqn. (22)]. The steric requirements of the reaction (22) will be higher as compared to those of reaction (20) and the observed small magnitudes of the steric reaction constants are thus consistent with the proposed acyclic mechanism. The formation of a cyclic transition state entails a more exacting specificity of orientation and should result in a much larger negative entropy of activation than that observed.

$$R-S-R' \; + \; CrO_2BrO^-pyH^+$$

(cyclic transition state structures) $\longrightarrow$ Products (22)

Techniques used: Spectrophotometry, correlation analysis

References: 41

Equations: 22

Table 1: Rate constants for the oxidation of methyl phenyl sulfide by PBC at 313 K

Table 2: Solvent effect on the oxidation of MeSPh by PBC at 293 K

Table 3: Dependence of the reaction rate on hydrogen-ion concentration

Table 4: Rate constants and activation parameters for the oxidation of sulfides by PBC

Table 5: Temperature dependence of the reaction constants for the oxidation of organic sulfides by PBC

Table 6: Correlation of rate of oxidation of alkyl phenyl sulfides with the Pavelich–Taft equation

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