

# Kinetics and mechanism of the oxidation of organic sulfides by quinolinium fluorochromate

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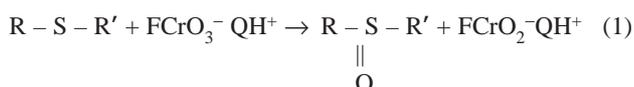
The oxidation of organic sulfides to corresponding sulfoxides by quinolinium fluorochromate proceeds through a sulfurane intermediate.

**Keywords:** organic sulfides, quinolinium fluorochromate

Quinolinium fluorochromate (QFC) has been reported as a synthetic reagent for the oxidation of alcohols to carbonyl compounds in 1992.<sup>1</sup> There seems to be no report on the oxidation of organic sulfides by QFC. We report here the kinetics of oxidation of 34 organic sulfides by QFC in *N,N*-dimethylformamide (DMF). Attempts have been made to correlate the structure and reactivity in the oxidation process.

QFC was prepared by the reported method.<sup>1</sup> Toluene-*p*-sulfonic acid (TsOH) was used as a source of hydrogen ions. The reactions were studied under pseudo-first-order conditions by keeping an excess ( $\times 15$  or greater) of the sulfide over QFC. The reactions were followed by monitoring the decrease in the concentration of QFC at 365 nm for up to 80% reaction extent. Pseudo-first-order rate constants,  $k_{\text{obs}}$ , were evaluated from linear plots ( $r > 0.995$ ) of  $\log [\text{QFC}]$  against time.

The oxidation of organic sulfides by QFC resulted in the formation of the corresponding sulfoxides. The overall reaction can be represented as equation (1) (Q = quinoline).



The reactions were found to be first order with respect to QFC. Michaelis-Menten type kinetics were observed with respect to substrate. This leads to the postulation of following overall mechanism and the rate law (4).



$$\text{Rate} = k_2 K [\text{sulfide}] [\text{QFC}]_t / (1 + K [\text{sulfide}]) \quad (4)$$

$$\text{Here, } [\text{QFC}]_t = [\text{QFC}] + [\text{Complex}]$$

The oxidation of methyl phenyl sulfide was studied in 19 organic solvents. The rate constants for oxidation,  $k_2$ , in 18 solvents ( $\text{CS}_2$  was not considered, as the complete range of solvent parameters was not available) did not exhibit significant correlation in terms of the linear solvation energy relationship equation (5) of Kamlet *et al.*<sup>16</sup>

$$\log k_2 = A_0 + p\pi^* + b\beta + a\alpha \quad (5)$$

The data on the solvent effect were analysed in terms of Swain's equation<sup>19</sup> of cation- and anion-solvating concept of the solvents as well.

$$\log k_2 = aA + bB + C \quad (11)$$

Here A represents the anion-solvating power of the solvent and B the cation-solvating power. C is the intercept term. (A + B) is postulated to represent the solvent polarity. The rates in different solvents were analysed in terms of equation (11), separately with A and B and with (A + B).

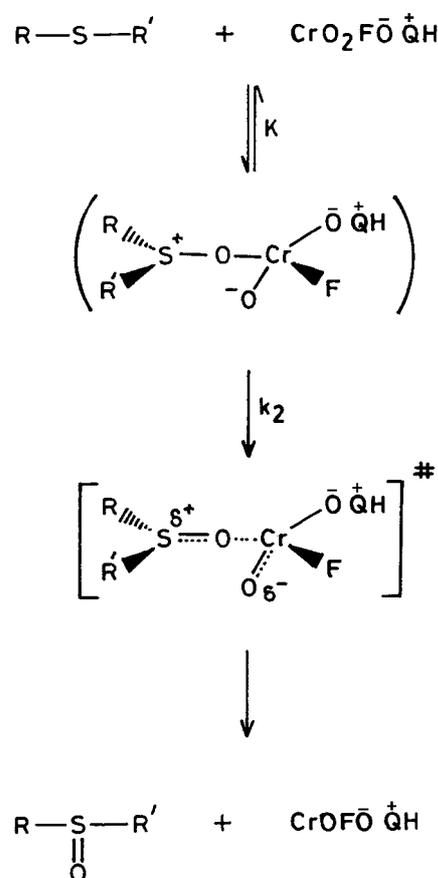
$$\log k_2 = 1.46 (\pm 0.02) A + 1.79 (\pm 0.01) B - 4.51 \quad (12)$$

$$R^2 = 0.9992; \text{sd} = 0.02; n = 19; \psi = 0.02$$

Here  $n$  is the number of data points and  $\psi$  is the Exner's statistical parameter.<sup>17</sup>

The rates of oxidation of methyl phenyl sulfide in the different solvents show an excellent correlation with Swain's equation with both the cation- and anion-solvating powers playing significant roles, though the contribution of the cation-solvation is slightly more than that of the anion-solvation.

*Correlation analysis of reactivity:* A perusal of data showed that the formation constants, K, of the intermediate complexes



Scheme 1

\* To receive any correspondence.

**Table 7** Temperature dependence of the reaction constants for the oxidation of organic sulfides by QFC

T/K	L	D	R	S	h	R <sup>2</sup>	sd	ψ	P <sub>D</sub>	P <sub>s</sub>	h
<i>para</i> -substituted ( <i>n</i> = 10)											
293	-1.32 ±0.02	-1.66 ±0.01	-1.35 ±0.07	-	0.81	0.9997	0.01	0.02	55.7	-	1.31
303	-1.24 ±0.02	-1.58 ±0.01	-1.31 ±0.07	-	0.81	0.9998	0.01	0.02	55.6	-	1.62
313	-1.19 ±0.01	-1.51 ±0.01	-1.23 ±0.05	-	0.81	0.9998	0.01	0.02	55.9	-	1.91
323	-1.12 ±0.02	-1.45 ±0.01	-1.24 ±0.07	-	0.85	0.9996	0.02	0.02	56.4	-	2.23
<i>meta</i> -substituted ( <i>n</i> = 8)											
293	-1.43 ±0.02	-1.25 ±0.02	-1.03 ±0.11	-	0.82	0.9998	0.01	0.02	46.6	-	1.27
303	-1.38 ±0.02	-1.19 ±0.01	-1.04 ±0.12	-	0.87	0.9997	0.01	0.02	46.3	-	1.57
313	-1.32 ±0.01	-1.17 ±0.01	-1.00 ±0.09	-	0.85	0.9998	0.01	0.02	46.7	-	1.88
323	-1.28 ±0.01	-1.12 ±0.01	-0.92 ±0.09	-	0.82	0.9997	0.01	0.02	46.7	-	2.18
<i>ortho</i> -substituted ( <i>n</i> = 10)											
293	-1.64 ±0.04	-1.67 ±0.03	-1.33 ±0.23	-0.98 ±0.04	0.80	0.9994	0.02	0.03	51.4	23.0	1.30
303	-1.58 ±0.02	-1.59 ±0.02	-1.22 ±0.12	-0.92 ±0.02	0.77	0.9994	0.02	0.03	50.1	22.5	1.60
313	-1.56 ±0.03	-1.49 ±0.02	-1.20 ±0.14	-0.84 ±0.03	0.81	0.9995	0.03	0.03	48.9	21.5	1.93
323	-1.53 ±0.05	-1.47 ±0.04	-1.20 ±0.28	-0.77 ±0.05	0.82	0.9989	0.03	0.04	49.0	20.4	2.21

do not exhibit much variation. However, the rate constants,  $k_2$ , of the disproportionation vary with the nature of substituent. The rate constants,  $k_2$ , were therefore subjected to correlation analysis.

Since the oxidation of aryl methyl sulfides failed to exhibit significant correlation with any single substituent-parameter or Taft's<sup>21</sup> dual substituent-parameter equations, the rate constants,  $k_2$ , were analysed in terms of Charton's<sup>23</sup> LDR/LDRS equations [equations (16) and (18)].

$$\log k_2 = L \sigma_1 + D \sigma_d + R \sigma_e + h \quad (16)$$

$$\log k_2 = L \sigma_1 + D \sigma_d + R \sigma_e + S \nu + h \quad (18)$$

Where  $\nu$  is the well-known Charton's steric parameter based on Van der Waals radii.<sup>24</sup>

The comparison of the L and D values for the substituted sulfides showed that the oxidation of *para*-substituted sulfides is more susceptible to the delocalisation effect than to the localised effect. However, the oxidation of *meta*-substituted compounds exhibited a greater dependence on the field effect. The oxidation of the *ortho*-compounds is almost equally susceptible to both the field and delocalisation effects.

All three regression coefficients, L, D and R, are negative indicating an electron-deficient sulfur centre in the transition state of the rate-determining step. The negative value of S indicates that the reaction is subject to steric hindrance by the *ortho*-substituent. This may be due to steric hindrance of the *ortho*-substituent to the approach of the oxidising species.

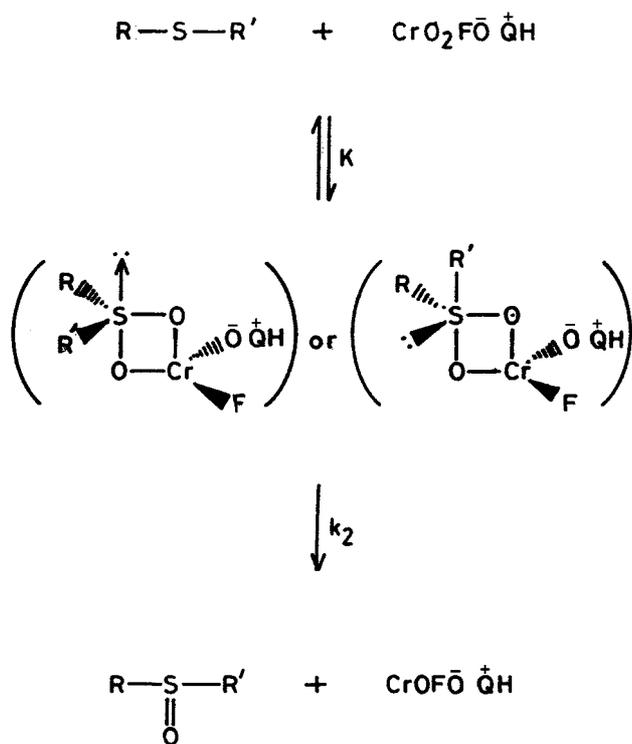
The rates of oxidation of alkyl phenyl sulfides did not yield any significant correlation separately with Taft's  $\sigma^*$  or  $E_s$  values. The rates were therefore analysed in terms of Pavelich-Taft's<sup>33</sup> dual substituent-parameter (DSP) equation (24).

$$\log k_2 = \rho^* \sigma^* + \delta E_s + \log k_0 \quad (24)$$

The correlations are excellent. Though the number of compounds is small (five) for any analysis by DSP equation, the results can be used qualitatively. The negative polar reaction constant confirms that the electron-donating power of the

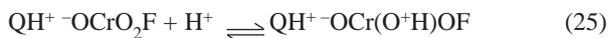
**Table 8** Correlation of rate of oxidation of alkyl phenyl sulfides by QFC in terms of the Pavelich-Taft equation

Temp/K	$\rho^*$	$\delta$	R <sup>2</sup>	sd	n
293	-2.35±0.09	0.75±0.02	0.9995	0.01	5
303	-2.16±0.06	0.70±0.01	0.9997	0.01	5
313	-2.04±0.09	0.67±0.02	0.9994	0.01	5
323	-1.89±0.10	0.60±0.02	0.9992	0.01	5



alkyl group enhances the reaction rate. The steric effect plays an inhibitory role.

The reaction is catalysed by hydrogen ions. The hydrogen-ion dependence has the form  $k_{\text{obs}} = a + b [\text{H}^+]$ . This suggests that the reaction follows two mechanistic pathways, one acid-independent and the other acid-dependent. The acid-catalysis can be attributed to a protonation of QFC to give a stronger oxidant and electrophile, equation (25).



The oxidation of methyl phenyl sulfide, in an atmosphere of nitrogen, failed to induce the polymerisation of acrylonitrile. Further, the addition of acrylonitrile had no effect on the rate of oxidation. Thus a one-electron oxidation, giving rise to free radicals, is unlikely.

The experimental results can be accounted for in terms of electrophilic oxygen transfer from QFC to the sulfide *via* an intermediate complex (Scheme 1), essentially similar to that suggested for oxidation of sulfides and iodide ions by periodate ion<sup>34</sup> and for the oxidation of sulfides by hydrogen peroxide<sup>25</sup> and PFC.<sup>14</sup> Low magnitudes of the polar reaction constants are consistent with the development of a polar transition state. Further, an electrophilic attack on the sulfide-sulfur is confirmed by the positive value of  $\eta$  which indicates that the substituent is better able to stabilise a cationic or electron-deficient site. The low magnitude of  $\eta$ , which represents the electronic demand of the reaction, indicates a less-pronounced charge separation in the transition state of the rate-determining step and supports a mechanism involving the formation of a polar transition state in the rate-determining step. The observed solvent effect also supports an  $\text{S}_{\text{N}}2$ -like transition state.

The oxidation of sulfides by QFC may involve a cyclic intermediate as has been suggested in many reactions of Cr(VI).<sup>35</sup> The cyclic transition state will be highly strained in view of the apical position of a lone pair of electrons or an alkyl group (Scheme 2). The steric requirements of Scheme 2 will be higher as compared to those of Scheme 1 and the observed small magnitudes of 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 much larger negative entropy of activation than that observed. The value of the entropy of activation obtained in this reaction is close to the

value observed in typical reactions involving oxygen transfer *e.g.* oxidation of iodide ion by periodate<sup>34</sup> and that of MeSPh by hydrogen peroxide,<sup>24</sup> periodate<sup>26</sup> and PFC<sup>14</sup> ( $\Delta S^\ddagger = -96, -115, -113, \text{ and } -89 \text{ J mol}^{-1} \text{ K}^{-1}$  respectively).

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Techniques used: Spectrophotometry, Correlation analysis

Equations: 25 Schemes: 2 References: 38

Table 1. Rate constants for the oxidation of methyl phenyl sulfide by QFC at 303 K

Table 2. Formation constants and thermodynamic parameters of sulfide-QFC complexes

Table 3. Rate constants of disproportionation and activation parameters of sulfide-QFC complexes

Table 4. Dependence of the reaction rate on hydrogen-ion concentration

Table 5. Solvent effect on the oxidation of MeSPh by QFC at 303 K

Table 6. Correlation analysis of the rates of oxidation of *meta*- and *para*-substituted organic sulfides by QFC with Taft's dual substituent-parameters at 293 K

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#### References cited in this synopsis

- 1 V. Murugesan and A. Pandurangan, *Ind. J. Chem.*, 1992, **31B**, 377.
- 16 M.J. Kamlet, J.L.M. Abboud, M.H. Abraham and R.W. Taft, *J. Org. Chem.*, 1983, **48**, 2877 and references cited therein.
- 17 O. Exner, *Collect. Czech. Chem. Commun.*, 1966, **31**, 3222.
- 19 C.G. Swain, M.S. Swain, A.L. Powel and S. Alunni, *J. Am. Chem. Soc.*, 1983, **105**, 502.
- 21 S.K. Dayal, S. Ehrenson and R.W. Taft, *J. Am. Chem. Soc.*, 1974, **94**, 9113.
- 23 M. Charton and B. Charton, *Bull. Soc. Chim. Fr.* 1988, 199 and references cited therein.
- 24 M. Charton, *J. Org. Chem.*, 1975, **40**, 407.
- 33 W.H. Pavelich and R.W. Taft, *J. Am. Chem. Soc.*, 1956, **79**, 4935.
- 35 Y.W. Chang and F.H. Westheimer, *J. Am. Chem. Soc.*, 1960, **82**, 1401; J. Rocek and F.H. Westheimer, *J. Am. Chem. Soc.*, 1962, **84**, 2241.