# Mechanism of Picolinic-acid-catalysed Chromium(VI) Oxidation of Alkyl Aryl and Diphenyl Sulphides

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The kinetics of picolinic acid (PA)-catalysed $Cr^{VI}$ oxidation of organic sulphur compounds have been studied with several alkyl aryl sulphides and diphenyl sulphides in acetic acid–water mixtures. The PA-catalysed oxidation follows third-order kinetics, first order each in oxidant, sulphide, and catalyst, at constant $[H^+]$ and ionic strength. A good correlation exists between log $k_2$ and Hammett $\sigma$ constants for both aryl methyl and diphenyl sulphides, and the reaction constants are negative. Steric congestion at the reaction centre, sulphur, has been revealed by studies with $C_6H_5SR$ (R = Me, Et, Pr, $Pr^i$, and $Bu^t$). Three mechanisms are proposed to account for the observed experimental results. In aryl methyl sulphides the rate benefit $(k_{cat} - k_{uncat})/k_{uncat}$ is the least for p-methoxyphenyl methyl sulphide and the largest for p-nitrophenyl methyl sulphide and this is in accordance with the reactivity–selectivity principle.

Though, in the chromium(VI) oxidation of organic compounds, reagents such as 1,10-phenanthroline, 2,2'-bipyridyl, and ethyl-enediaminetetra-acetic acid (EDTA) act as efficient catalysts,[1,2] Rocek and Peng[3] were the first to report that picolinic acid (PA) is a specific catalyst for the $Cr^{VI}$ oxidation of alcohols. In the PA-catalysed $Cr^{VI}$ oxidation of propan-2-ol the rate acceleration has been attributed to fast attack of PA-complexed $Cr^{VI}$ on the alcohol. Our interest in the oxidation of organic sulphur compounds by several oxidants,[4–8] and in particular our recent studies on the uncatalysed $Cr^{VI}$ oxidation of organic sulphides,[9] prompted us to undertake a detailed investigation on the kinetics of PA-catalysed $Cr^{VI}$ oxidation of a number of alkyl aryl sulphides and a few diphenyl sulphides in acetic acid–water mixtures. Incidentally this study appears to be the first report on the effect of substituents in PA-catalysed $Cr^{VI}$ oxidations.

## Results and Discussion

The constant values of first-order rate constants $(k_1)$ at different initial $[Cr^{VI}]$ and the constant second-order rate constants $(k_2)$ for different initial concentrations of methyl phenyl sulphide (MPS) (see Table 1) reveal that the reaction is first order each in the oxidant and the sulphide. This has also been corroborated by the observations that (i) the plot of log $(a - x)$ *versus* time is linear for each kinetic run $(r > 0.995)$ and (ii) the linear plot of $k_1$ *versus* [MPS] passes through the origin $(r\ 0.997)$. The data in Table 1 clearly show that the rate order in PA is also one. As the half-life of the reaction is only a few minutes, the iodimetric procedure used to follow the kinetics of the reaction did not permit us to extend the study to a large concentration range of the reactants. It is interesting to note that in the presence of $1.50 \times 10^{-3}$ mol dm$^{-3}$ PA (three times the concentration of the oxidant) the oxidation is *ca.* twelve times faster than that in its absence (Table 1), which is comparable to the rate acceleration (20-times) observed in the oxidation of propan-2-ol when [PA] is five times that of $[Cr^{VI}]$.

The reaction rate increases with an increase in the hydrogen ion concentration (Table 2) (in evaluating $[H^+]$ the dissociation of acetic acid was also taken into account) which could be studied only over a narrow range. The change of ionic strength has no influence on the reaction rate. An increase in the percentage of acetic acid in the medium enhanced the rate of oxidation (Table 2) and this may be attributed to the increased
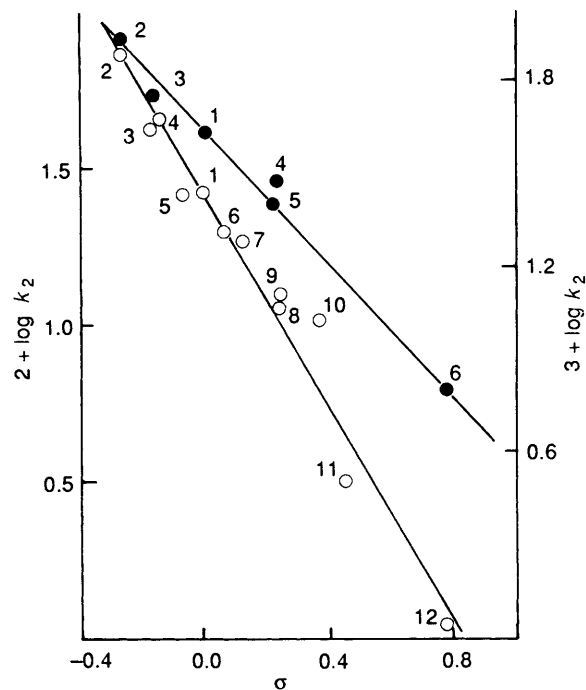


**Figure.** Hammett plots for aryl methyl and diphenyl sulphides at 313 K: aryl methyl sulphides (○); diphenyl sulphides (●). The points in the figure are referred to by the same numbers as the substituents in Table 3 for aryl methyl sulphides and Table 5 for diphenyl sulphides.

acidity of the medium. The above observations are quite similar to those observed in the uncatalysed $Cr^{VI}$ oxidation of sulphides.[9]

A study of the effect of substituents on the rates of PA-catalysed oxidation (Table 3) indicates that in aryl methyl sulphides electron-donating substituents in the benzene ring accelerate the rate whereas electron-withdrawing groups retard it. The second-order rate constants are several times larger than those of the uncatalysed reactions for all the sulphides studied here. A satisfactory correlation exists between log $k_2$ and the Hammett $\sigma$ constants at the three temperatures studied, and a representative Hammett plot at 40 °C is given in the Figure. The negative Hammett slope ($\rho$ $-1.66 \pm 0.23$, $r$ 0.982, $s$ 0.10, $n$

**Table 1.** Pseudo-first-order ($k_1$) and second-order ($k_2$) rate constants for the PA-catalysed $Cr^{VI}$ oxidation of MPS in 50% (v/v) aq. acetic acid at 303 K; [$HClO_4$] 0.001 mol dm$^{-3}$; $I$ = 0.02 mol dm$^{-3}$.

| [MPS]/10$^{-2}$ mol dm$^{-3}$ | [Cr$^{VI}$]/ mmol dm$^{-3}$ | [PA]/mmol dm$^{-3}$ | $k_1$ $^a$/10$^{-3}$ s$^{-1}$ | $k_2$/10$^{-1}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $\frac{k_1}{[PA]}$/10$^{-1}$ dm$^3$ mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|---|---|
| 0.500 | 0.500 | 1.00 | 0.969 ± 0.07 | 1.94 ± 0.14 | 0.969 ± 0.07 |
| 0.750 | 0.500 | 1.00 | 1.38 ± 0.31 | 1.84 ± 0.41 | |
| 1.00 | 0.500 | 1.00 | 1.67 ± 0.33 | 1.67 ± 0.33 | |
| 1.25 | 0.500 | 1.00 | 2.13 ± 0.38 | 1.70 ± 0.30 | |
| 1.50 | 0.500 | 1.00 | 2.58 ± 0.50 | 1.72 ± 0.33 | |
| 0.500 | 0.250 | 1.00 | 1.09 ± 0.10 | 2.18 ± 0.20 | |
| 0.500 | 0.400 | 1.00 | 1.01 ± 0.12 | 2.02 ± 0.24 | |
| 0.500 | 0.500 | 0.00 | 0.125 ± 0.01 | | |
| 0.500 | 0.500 | 1.25 | 1.28 ± 0.20 | 2.56 ± 0.40 | 1.02 ± 0.16 |
| 0.500 | 0.500 | 1.50 | 1.53 ± 0.15 | 3.06 ± 0.30 | 1.02 ± 0.10 |

$^a$ The error quoted in $k$ is the 95% confidence limit of Student's $t$-test.

**Table 2.** Effect of varying [$H^+$], $I$, and percentage of solvent composition on the oxidation of MPS at 303 K; [MPS] 0.005 mol dm$^{-3}$; [$Cr^{VI}$] 0.0005 mol dm$^{-3}$; [PA] 0.001 mol dm$^{-3}$.

| [H$^+$]/10$^{-2}$ mol dm$^{-3}$ | $k_1$/10$^{-3}$ s$^{-1}$ | $\frac{k_1}{[H^+]}$/10$^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $I$/10$^{-2}$ dm$^3$ mol$^{-1}$ | $k_1$/10$^{-3}$ s$^{-1}$ | AcOH–water % (v/v) | $k_1$/10$^{-3}$ s$^{-1}$ |
|---|---|---|---|---|---|---|
| 4.79 | 0.969 ± 0.01 | 2.02 ± 0.02 | 0.250 | 1.04 ± 0.17 | 40–60 | 0.652 ± 0.12 |
| 5.01 | 1.02 ± 0.01 | 2.04 ± 0.02 | 2.00 | 0.969 ± 0.01 | 50–50 | 0.969 ± 0.01 |
| 6.46 | 1.38 ± 0.14 | 2.14 ± 0.20 | 5.00 | 1.09 ± 0.15 | 60–40 | 1.34 ± 0.17 |
| 8.71 | 1.88 ± 0.03 | 2.16 ± 0.03 | | | 70–30 | 2.03 ± 0.09 |

**Table 3.** Second-order rate constants and enthalpies and entropies of activation for the PA-catalysed $Cr^{VI}$ oxidation of $XC_6H_4SMe$ in 50% (v/v) aq. acetic acid [$Cr^{VI}$] 0.0005 mol dm$^{-3}$, [PA] 0.001 mol dm$^{-3}$, [$HClO_4$] 0.001 mol dm$^{-3}$, $I$ = 0.02 mol dm$^{-3}$.

| Entry | X | $k_2$/10$^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ 303 K | 313 K | 323 K | $\Delta H^{\ddagger}$/kJ mol$^{-1}$ $^a$ | $-\Delta S^{\ddagger}$/J K$^{-1}$ mol$^{-1}$ $^a$ |
|---|---|---|---|---|---|---|
| 1 | H | 19.4 ± 1.4 | 27.1 ± 1.0 (3.11 ± 0.07)$^b$ | 30.1 ± 3.5 | 15.4 ± 6.3 (25.9 ± 2.8) | 208 ± 21 (192 ± 9.6) |
| 2 | p-OMe | 53.6 ± 6.7 | 74.6 ± 1.2 (19.9 ± 1.6) | 80.8 ± 6.0 | 14.2 ± 9.2 (37.6 ± 6.7) | 203 ± 31 (139 ± 23) |
| 3 | p-Me | 36.3 ± 3.8 | 43.1 ± 4.2 (5.85 ± 0.29) | 55.0 ± 6.0 | 14.7 ± 8.4 (26.1 ± 4.4) | 205 ± 29 (186 ± 15) |
| 4 | p-Pr$^i$ | 37.2 ± 3.3 | 46.0 ± 6.2 (5.25 ± 0.19) | 52.9 ± 6.4 | 11.8 ± 9.2 (27.4 ± 3.6) | 215 ± 31 (183 ± 12) |
| 5 | m-Me | 21.0 ± 1.8 | 26.6 ± 2.0 (3.33 ± 0.16) | 30.8 ± 6.1 | 13.6 ± 9.6 (27.1 ± 4.1) | 215 ± 33 (187 ± 14) |
| 6 | p-F | 16.7 ± 1.6 | 20.6 ± 2.0 (2.56 ± 0.13) | 25.0 ± 2.7 | 13.0 ± 8.2 (27.9 ± 3.2) | 214 ± 28 (187 ± 11) |
| 7 | m-OMe | 13.5 ± 1.7 | 18.9 ± 1.3 (2.15 ± 0.10) | 20.8 ± 3.3 | 15.1 ± 9.6 (28.2 ± 3.3) | 212 ± 33 (187 ± 11) |
| 8 | p-Cl | 9.05 ± 0.97 | 11.9 ± 1.7 (1.41 ± 0.07) | 19.0 ± 1.5 | 27.6 ± 8.8 (27.4 ± 3.7) | 174 ± 30 (193 ± 13) |
| 9 | p-Br | 8.21 ± 1.3 | 12.1 ± 1.4 (1.29 ± 0.04) | 19.9 ± 0.83 | 33.4 ± 8.8 (27.7 ± 2.9) | 155 ± 30 (193 ± 9.9) |
| 10 | m-Cl | 8.83 ± 0.63 | 10.6 ± 0.76 (0.668 ± 0.02) | 12.5 ± 1.1 | 13.3 ± 6.3 (25.2 ± 3.5) | 227 ± 21 (207 ± 12) |
| 11 | p-CO$_2$H | 2.04 ± 0.26 | 3.25 ± 0.36 (0.298 ± 0.02) | 4.99 ± 0.48 | 33.9 ± 9.1 (27.1 ± 4.2) | 166 ± 31 (207 ± 14) |
| 12 | p-NO$_2$ | 0.793 ± 0.08 | 1.11 ± 0.09 (0.068 ± 0.01) | 2.01 ± 0.33 | 35.2 ± 9.2 (19.8 ± 6.7) | 170 ± 31 (243 ± 23) |

$^a$ The precision of the $\Delta H^{\ddagger}$- and $\Delta S^{\ddagger}$-values was calculated by using the method of Petersen et al.[17] $^b$ The values in parentheses correspond to the uncatalysed reactions under similar conditions, and were obtained from ref. 9.

12) shows that the nucleophilic sulphur atom of the sulphide is more positively charged in the transition state than it is in the reactant. The lower magnitude of $\rho$ in the catalysed oxidation ($\rho$ $-1.66 \pm 0.23$ at 40 °C) in comparison with the uncatalysed one ($\rho$ $-2.11 \pm 0.23$ at 40 °C) demonstrates the low selectivity of the catalysed reaction. Though the negative $\rho$-value indicates a considerable degree of sulphonium ion character in the transition state, the magnitude of the reaction constant is smaller than those observed in the reactions proceeding via halogenosulphonium cations.[10,11] Therefore, in the transition state of this reaction the electron deficiency on the sulphur atom may not be very high, but may be similar to those in the oxidation of sulphides by hydrogen peroxide[12] ($\rho$ $-1.13$), peroxyhexanoylnitrate[13] ($Me[CH_2]_4Co_2ONO_2$; $\rho$ $-1.70$), periodate ion[14] ($\rho$ $-1.40$), permanganate ion[15] ($\rho$ $-1.36$), and pyridinium fluorochromate[16] ($\rho$ $-1.50$).

The activation parameters in Table 3 for uncatalysed and PA-catalysed $Cr^{VI}$ oxidation of sulphides reveal that the higher reactivity of PA-catalysed oxidation is mainly due to enthalpic factors. The Petersen's error criterion[17] is satisfied in the present study, i.e. $\Delta\Delta H^{\ddagger}$ (23.4 kJ mol$^{-1}$) > 2$\partial$ (19.2 kJ mol$^{-1}$) (where $\partial$ is the calculated maximum possible error) and hence the correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is significant. This significant correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ is statistically satisfactory (isokinetic temperature, $\beta$, slope 385 ± 72 K, $r$ 0.966) indicating that the PA-catalysed oxidation occurs by a similar mechanism for all aryl methyl sulphides.

Studies with different alkyl phenyl sulphides show that the rate decreases in the order PhSMe > PhSEt > PhSPr$^n$ > PhSPr$^i$ > PhSBu$^t$ {the second-order rate constants, $10^2k_2$ dm$^3$ mol$^{-1}$ s$^{-1}$, 27.1 ± 1.0, 20.7 ± 2.6, 19.0 ± 1.9, 12.6 ± 2.0, and 2.59 ± 0.38 at 40 °C respectively. [$Cr^{VI}$] 0.0005 mol dm$^{-3}$;

[sulphide] 0.005 mol dm$^{-3}$; [PA] 0.001 mol dm$^{-3}$; [HClO$_4$] 0.001 mol dm$^{-3}$; $I$ 0.02 mol dm$^{-3}$; solvent 50% (v/v) aq. acetic acid}. A good correlation of log($k_2/k_2$Me) with $E_s$, Taft's steric substituent constant ($r$ 0.991, $s$ 0.06, slope 0.650 $\pm$ 0.16), for the alkyl phenyl sulphides demonstrates that a steric effect seems to play a significant role in the catalysed oxidation, *i.e.* as the bulkiness of the alkyl group increases, there will be hindrance of the formation of the transition state (4) or (5) (*vide infra*).

Investigations with diphenyl sulphide (DPS) show that the reaction is first order in Cr$^{VI}$, DPS (constant $k_2$-values at varying [DPS], Table 4) and in PA (constant $k_3$-values, Table 4). The variations in the rates of oxidation of DPS brought about by an increase in [HClO$_4$], change in ionic strength, and solvent composition are almost identical with those observed for MPS. The rate data (Table 5) of 4-substituted diphenyl sulphides give excellent correlation with $\sigma$ (a representative plot is given in Figure 1, $\rho_{cat}$ $-1.00 \pm 0.17$ at 40 °C; $\rho_{uncat}$ $-1.80 \pm 0.26$ at 40 °C). An excellent correlation exists between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ ($r$ 0.998) in the catalysed oxidation of diphenyl sulphides, the data satisfy Petersen's error criterion, and the value of $\beta$ is 380 $\pm$ 30 K which is very close to the value observed for aryl methyl sulphides. A plot of log $k_2$ of diphenyl sulphides *versus* log $k_2$ of the aryl methyl sulphides at 40 °C is linear ($r$ 0.997), indicating that the two series of sulphides follow a similar mechanism in PA-catalysed Cr$^{VI}$ oxidation.

*Mechanism and Rate Law of PA-catalysed Oxidation.*—The active oxidising species of Cr$^{VI}$ under our experimental conditions is the acid chromate ion, HCrO$_4^-$.[18] PA is a weak base and is protonated as shown in equation (1). PA readily forms a reactive Cr$^{VI}$ complex (1) by reaction with HCrO$_4^-$ [equation (2)] and the cyclic structure of intermediate (1) has been established by the observation that only pyridine-2-carboxylic acid and pyrazine-2-carboxylic acid show significant catalytic effect in the oxidation of alcohols under these conditions.[3]



(1)



(2)
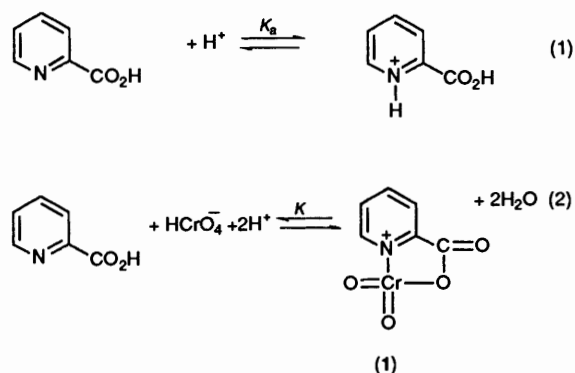
To account for the foregoing experimental observations, three mechanisms may be envisaged.

In Scheme 1, the cyclic complex (1) reacts with a molecule of MPS to give the sulphide cation radical (2) and Cr$^{VI}$–PA complex (3) in the rate-limiting step, equation (3). This is followed by a subsequent fast step in which the radical cation (2) readily attacks the Cr–O bond in complex (3) to yield intermediate (4) [equation (4)]. This is analogous to the mechanism proposed by Wiberg[18] in the diacetyl chromate oxidation of diphenyl sulphide where an electron transfer from sulphur to Cr$^{VI}$ followed by an attack of the sulphide radical cation on the Cr–O bond of the oxidant has been suggested from ^{18}O-labelling studies. Scheme 1 is similar to that proposed for the uncatalysed Cr$^{VI}$ oxidation of sulphides[9] and sulphoxides.[19] As in the uncatalysed oxidation, in the PA-
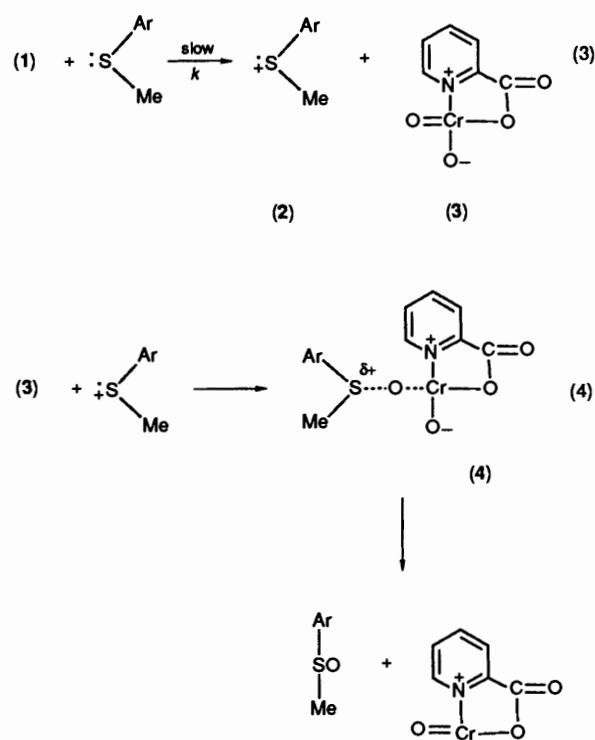


Scheme 1.

catalysed reactions we observed a good correlation between log $k_2$ and oxidation potential and/or first ionization energies. The initial nucleophilic attack of sulphide on the oxygen of Cr$^{VI}$–PA complex (Scheme 2) can also yield intermediate (4) in the transition state.
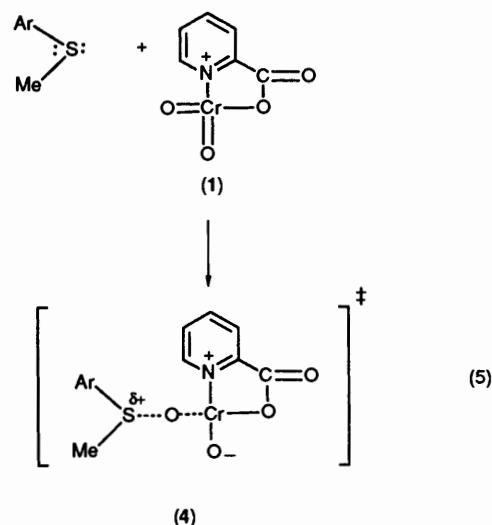


Scheme 2.

Another mechanism (Scheme 3), involving nucleophilic attack of the sulphide on the chromium of species (1) with the formation of the transition state (5), may also be possible [equation (6)]. The subsequent ligand coupling of O$^-$ and S leads to the formation of sulphoxide and Cr$^{IV}$–PA complex [equation (7)]. Though such ligand coupling is not a familiar reaction, recently Oae *et al.*[20–22] have advocated its occurrence in the reaction of benzyl 2-pyridyl and related sulphoxides with Grignard reagents. It may be pointed out here that in the pyridinium chlorochromate oxidation of aliphatic and diphenyl

**Table 4.** Pseudo-first-order and second-order rate constants for the PA-catalysed $Cr^{VI}$ oxidation of DPS in 75% acetic acid–25% water (v/v) at 303 K; $[HClO_4]$ 0.02 mol dm$^{-3}$.

| [DPS]/10$^{-2}$ mol dm$^{-3}$ | [Cr$^{VI}$]/mmol dm$^{-3}$ | [PA]/mmol dm$^{-3}$ | $k_1/10^{-4}$ s$^{-1}$ | $k_2/10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | $k_3$/dm$^6$ mol$^{-2}$ s$^{-1}$ |
|---|---|---|---|---|---|
| 0.500 | 0.500 | 1.00 | 11.3 ± 1.9 | 22.0 ± 3.8 | 220 ± 38 |
| 0.600 | 0.500 | 1.00 | 13.9 ± 2.1 | 23.2 ± 3.6 | 232 ± 36 |
| 0.800 | 0.500 | 1.00 | 17.5 ± 2.8 | 21.9 ± 3.5 | 219 ± 35 |
| 0.500 | 0.500 | 1.50 | 13.7 ± 2.4 | 27.4 ± 4.8 | 183 ± 32 |
| 0.500 | 0.500 | 2.00 | 20.1 ± 4.5 | 20.1 ± 9.0 | 201 ± 45 |

**Table 5.** Second-order rate constants and enthalpies and entropies of activation for PA-catalysed $Cr^{VI}$ oxidation of $XC_6H_4SPh$ in 75% acetic acid–25% water (v/v); [Cr$^{VI}$] 0.0005 mol dm$^{-3}$; [PA] 0.001 mol dm$^{-3}$; $[HClO_4]$ 0.02 mol dm$^{-3}$.

| Entry | X | $k_2/10^{-2}$ dm$^3$ mol$^{-1}$ s$^{-1}$ | | | $\Delta H^{\ddagger}$/kJ mol$^{-1}$ | $-\Delta S^{\ddagger}$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|---|---|---|
| | | 303 K | 313 K | 323 K | | |
| 1 | H | 21.9 ± 2.4 | 41.7 ± 3.9 (3.50 ± 0.10)$^a$ | 59.6 ± 5.1 | 38.3 ± 7.8 | 150 ± 27 |
| 2 | 4-OMe | 52.6 ± 2.4 | 80.4 ± 10 (7.72 ± 0.31) | 111 ± 13 | 27.7 ± 9.6 | 178 ± 33 |
| 3 | 4-Me | 35.2 ± 3.9 | 55.0 ± 2.4 (6.91 ± 0.28) | 77.7 ± 7.9 | 29.7 ± 6.8 | 175 ± 23 |
| 4 | 4-Cl | 16.3 ± 1.7 | 29.8 ± 2.3 (1.47 ± 0.22) | 42.1 ± 4.8 | 36.2 ± 8.0 | 160 ± 27 |
| 5 | 4-Br | 14.3 ± 0.9 | 25.4 ± 3.2 (1.39 ± 0.04) | 46.0 ± 4.9 | 45.0 ± 7.9 | 132 ± 27 |
| 6 | 4-NO$_2$ | 2.59 ± 0.2 | 6.41 ± 0.4 (0.11 ± 0.01) | 12.6 ± 0.70 | 62.0 ± 7.9 | 89.9 ± 27 |

$^a$ The values in parentheses at 313 K correspond to rate constants for uncatalysed reactions under similar conditions.



(5)
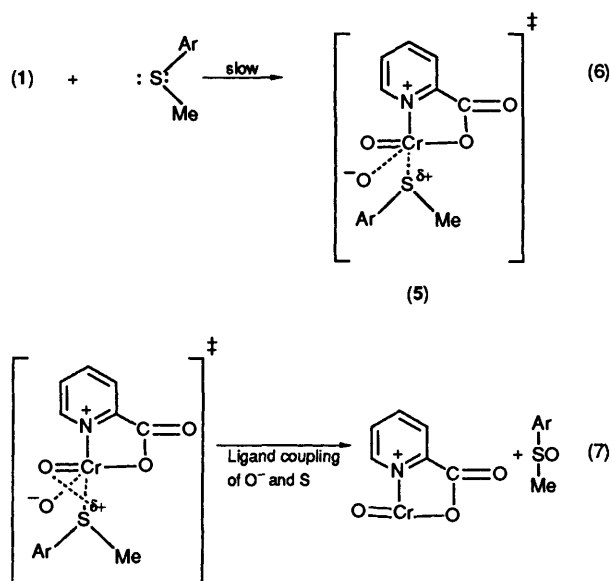


**Scheme 3.**

sulphides, Panigrahi and Mahapatro[23] have not only postulated the formation of $\overset{+}{S}$–$\overset{-}{O}$ species, but also a $\overset{+}{S}$–Cr-linkage formed by attack of the sulphur on chromium.

Thus, the rate-limiting step may involve one-electron transfer (Scheme 1) or a nucleophilic attack of the sulphide on the oxygen of species (1) (Scheme 2) or on the chromium of species (1) (Scheme 3). The Hammett ρ-value of −1.66 for the PA-catalysed oxidation of aryl methyl sulphides, and the good correlation of the rates of alkyl phenyl sulphides with $E_s$-values, may favour the nucleophilic attack of the sulphide on the oxygen of species (1) [equation (5)] or the chromium of species (1) [equation (6)] rather than the one-electron transfer from the sulphide to the oxidant. A typical electrophilic oxidation of the sulphide ArSMe with $H_2O_2$,[12] $IO_4^-$,[14] $MnO_4^-$,[15] and peroxyhexanoyl nitrate[13] has reaction constants in the range of −1.1 to −1.7, whereas in a typical one-electron-transfer reaction as found in the oxygenation with cytochrome P-450

and other $\overset{+\bullet}{S}$-forming reactions investigated by Watanabe et al.[24] and Ando and coworkers[25] the rates are much better correlated with σ$^+$ rather than σ, and ρ$^+$-values are in the range −0.1 to −0.2. However, the present kinetic data cannot allow us to discriminate among the proposed mechanisms. Hence the possible mechanisms are the nucleophilic attack of sulphide to the oxygen or the chromium or electron transfer to $Cr^{VI}$–PA complex. However, it is pertinent to point out that Ruff and Kucsman[10] observed a value of −4.25 as the reaction constant for the reaction of aryl methyl sulphides with TsNHCl, wherein a chlorosulphonium ion intermediate has been postulated. Miotti et al.[11] have reported a value of −3.2 for the bromine oxidation of sulphides proceeding via a bromosulphonium ion intermediate. In the proposed mechanisms (Schemes 1–3), the end product has been shown as the $Cr^{IV}$–PA complex. This complex reacts rapidly with a sulphide molecule to yield a $Cr^{III}$–PA complex and a sulphide cation radical, which in turn will reduce another molecule of $Cr^{VI}$–PA complex to a $Cr^{V}$–PA complex. The $Cr^{V}$–PA complex will react with another molecule of sulphide to form sulphoxide and $Cr^{III}$–PA complex. Thus the proposed schemes account for the observed stoicheiometry (see Experimental section).

The following rate laws [equation (8) and (9)] can be derived from Schemes 1–3.

$$\text{rate} = k[\text{sulphide}][(1)] \tag{8}$$

$$= Kk[\text{sulphide}][HCrO_4^-][PA][H^+]^2 \tag{9}$$

The total PA concentration is given by equation (10) where

$$[PA_T] = [PA] + [PAH^+] \tag{10}$$

$[PA_T]$, $[PA]$, and $[PAH^+]$ represent the total, free, and protonated picolinic acid. It can be shown that equation (11) holds.

$$[PA] = \frac{[PA_T]K_a}{K_a + [H]} \tag{11}$$

Substituting equation (11) into equation (9) we get rate equation (12).

**Table 6.** Rate benefit in the PA-catalysed $Cr^{VI}$ oxidation of aryl methyl sulphides in 50% (v/v) aq. acetic acid at 313 K; $[Cr^{VI}]$ 0.0005 mol $dm^{-3}$; [ArSMe] 0.005 mol $dm^{-3}$, [PA] 0.001 mol $dm^{-3}$, $[HClO_4]$ 0.001 mol $dm^{-3}$.

| Substituent | $(k_{cat} - k_{uncat})/k_{uncat}$ |
|---|---|
| H | 7.71 |
| $p$-OMe | 2.75 |
| $p$-Me | 6.37 |
| $p$-$Pr^i$ | 7.76 |
| $m$-Me | 6.99 |
| $p$-F | 7.05 |
| $m$-OMe | 7.79 |
| $p$-Cl | 7.44 |
| $p$-Br | 8.38 |
| $m$-Cl | 14.9 |
| $p$-$CO_2H$ | 9.91 |
| $p$-$NO_2$ | 15.3 |

$$\text{rate} = \frac{KK_a k[PA_T][HCrO_4^-][\text{Sulphide}][H^+]^2}{K_a + [H^+]} \quad (12)$$

At constant $[H^+]$, equation (12) reduces to equation (13).

$$\text{rate} = k_3[\text{sulphide}][HCrO_4^-][PA_T] \quad (13)$$

Equation (13) explains the observed kinetic features of the catalysed oxidation.

*Comparison with the Uncatalysed $Cr^{VI}$ Oxidation of Sulphides.*—As already indicated for both *meta-* and *para*-substituted phenyl methyl sulphides, the second-order rate constants are several times higher than those of the uncatalysed reactions (see Table 3). The log–log plot of the second-order rate constants of the PA-catalysed and uncatalysed $Cr^{VI}$ oxidations of aryl methyl sulphides at 40 °C is linear ($r$ 0.998, $s$ 0.008, slope 0.80), indicating that the transition states of the two reactions are related to each other. The rate benefit due to the catalyst is represented by the quotient $(k_{cat} - k_{uncat})/k_{uncat}$. Values for this function for the various sulphides are collected in Table 6. The rate gain depends on the reactivity of the sulphide employed in the oxidation. For a more reactive sulphide such as $p$-methoxyphenyl methyl sulphide the quotient is lower than that observed for a less reactive sulphide such as $p$-nitrophenyl methyl sulphide. This behaviour is in accordance with the reactivity–selectivity principle which states that a more reactive species will be less selective in choosing its reaction partner and *vice versa*.[26]

## Experimental

PA was used after repeated recrystallisation from methanol. All the alkyl aryl sulphides and diphenyl sulphides have been prepared by known procedures [4,9,27–30] and purity was checked by the usual methods. All the other chemicals employed were of AR/GR grade or were purified by standard procedures.[31] In PA-catalysed $Cr^{VI}$ oxidations the kinetic studies were carried out under pseudo-first-order conditions in 50% acetic acid–50% water (v/v) mixture with alkyl aryl sulphides, and in 75% acetic acid–25% water (v/v) mixture with diphenyl sulphides. Similar conditions were employed in uncatalysed $Cr^{VI}$ oxidations of sulphides.[9] The titrimetric procedure of Wiberg and Mill [32] was followed for the estimation of unchanged $Cr^{VI}$ as described earlier. The method of calculation of rate constants $k_1$, $k_2$ and

activation parameters and their precision are described in our previous report.[4] The product of this reaction is the corresponding sulphoxide and the stoicheiometry of the oxidation is similar to that of the uncatalysed oxidation, *i.e.* three molecules of sulphide are oxidised for each two $Cr^{VI}$ species reduced to $Cr^{III}$.

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