Kinetics of oxidation of organic sulphides with carboxylato-bound chromium(V)

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Carboxylato-bound Cr(V) oxidation of aryl methyl sulphides (ArSMe) proceeds through a complex formation between the oxidant and substrate. The peculiar substituent effect observed is attributed to the reaction being carried out at a temperature close to the isokinetic temperature. Comparison of the kinetic results observed with Cr(V) and Cr(VI) oxidations points out the operation of different mechanisms—single electron transfer in Cr(VI) oxidation and complex formation followed by ligand coupling in Cr(V) oxidation.

Though a large variety of reagents have been utilized for the oxidation of organic sulphides, only a limited number of reports, that too recently, have appeared using transition metal-based oxidants1-7. A few reports have appeared from this laboratory on the mechanism of metal ion oxidation of organic sulphur compounds and the authors observed very interesting results on the uncatalyzed and catalyzed chromium(VI) oxidation of aryl aryl sulphones2,8-11. The proposed mechanisms speculated Cr(V) and Cr(IV) as intermediates in the Cr(VI) oxidation of organic sulphides2,10.

Though Cr(VI) is a very stable and well established oxidant, Cr(V) undergoes disproportionation unless incorporated into chelates of hydroxy-carboxylic acids, schwiff bases or sugars1,12. Thus the intermediate Cr(V) and Cr(IV) states, which existed only transiently in the Cr(VI) oxidations of several organic and inorganic substrates, can be stabilized by chelation. The recent interest in the less usual IV and V oxidation states of chromium reflects the importance of these species in inorganic redox mechanisms, in biosystems and in the carcinogenic activity of chromium compounds12-14.

Recently, complexes of Cr(V) with carboxylate and schwiff base ligands have been isolated in which the oxidation state is stable enough to permit spectroscopic and crystallographic studies12-16. Further it has been proved that the major structural change in the redox series Cr(V, IV, III) is associated with its 5+/4+ component17. Herein we report our results on the kinetics of carboxylato bound Cr(V) oxidation of several aryl methyl sulphides. The results obtained in the present study are compared with the Cr(VI) oxidation of organic sulphides2.

Materials and Methods
Sodium bis(2-ethyl-2-hydroxybutanato)-oxochromium(V) (I) was synthesized from 2-ethyl-2-hydroxybutanoic acid (HEBA) (Aldrich 99%) and sodium dichromate (Merck) in acetone (Merck, AR grade) as described earlier17. Crystallization of the product was induced by dropwise addition of hexane over a period of 10-15 min. The aryl methyl sulphones were synthesized by standard procedures and purity checked by spectral methods2,10,11. Acetonitrile was purified before use and doubly distilled water was used throughout the course of the reaction. All other reagents were of AnalR grade.

The kinetics of the reaction was followed by measuring absorbance changes at 540 nm of Cr(V) employing Hitachi-200 UV-visible spectrophotometer. Though the absorption maximum for the Cr(V) complex in aqueous solution is 510 nm, in the presence of acetonitrile the λ_max is shifted to 540 nm. Similar shift in λ_max due to the change of the medium to acetonitrile was noticed by Rajavelu and Srinivasan in the Cr(V) oxidation of lactic and thiolactic acids18. In all the cases, at least a 10-fold stoichiometric excess of substrate over the
oxidant was used to ensure pseudo-first order conditions. Rate constants were evaluated by using semilogarithmic plots of absorbance differences versus reaction time by least squares method. Duplicate kinetic runs showed that the rate constants were reproducible to within ±5%. The error quoted in k is the 95% confidence limit of student's t-test. The thermodynamic parameters, \( \Delta H^\ddagger \) and \( \Delta S^\ddagger \), have been evaluated from the slope and intercept of the Eyring plot of \( \log k/T \) versus \( 1/T \).

Results and Discussion

Kinetics of oxidation of sulphides with Cr(V) have been followed spectrophotometrically under pseudo-first order conditions in aqueous acetonitrile (50:50 v/v) by taking an excess of substrate over oxidant. The oxidation of methyl phenyl sulphide (MPS) at 23°C is first order in oxidant, Cr(V), as evidenced from the linearity of log \( (A_o - A_t) \) versus time plots, as well as the constancy of first order rate constants, \( k_1 \), at different [Cr(V)]. Variation of [MPS] at constant [Cr(V)] resulted in variation of the \( k_1 \) values (Table 1). The calculated second order rate constant values \( k_2 = k_1/[\text{MPS}] \) decreased with increase in [substrate] indicating that the order in substrate is different from unity. The dependence of rate of oxidation on [substrate] has also been tested in several para-substituted phenyl methyl sulphides. The \( k_1 \) and \( k_2 \) values (calculated from \( k_2 = k_1/[\text{substrate}] \)) at different [substrate] for \( p\)-MeC_6H_4SMe and \( p\)-NO_2C_6H_4SMe are given in Table 2. Similar results have been observed for other para-substituted phenyl methyl sulphides also. Though the \( k_2 \) value varies with the nature of the substituent in the phenyl ring of ArSMe, in all cases the value decreases with increase in [substrate]. The observed saturation in the reaction rate at high [sulphide] can be interpreted in terms of reversible formation of a Cr(V)-sulphide complex (Eq. 2). If electron transfer from sulphide to Cr(V) is the rate determining step then Cr(IV) is one of the products. As we are not able to notice any increase in absorbance either at 540 nm or 600 nm, the formation of Cr(IV) as intermediate is unlikely\(^1\). The Cr(V)-sulphide complex II undergoes decomposition to

<table>
<thead>
<tr>
<th>[Oxidant] = 0.001 M</th>
<th>[H^+] = 0.01 M</th>
<th>[C_6H_5SMe]</th>
<th>Cr(V) oxidation</th>
<th>Cr(VI) oxidation*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_1 \times 10^4 \text{(s}^{-1}) )</td>
<td>( k_2 \times 10^2 \text{(M}^{-1} \text{s}^{-1}) )</td>
<td>( k_1 \times 10^5 \text{(s}^{-1}) )</td>
<td>( k_2 \times 10^3 \text{(M}^{-1} \text{s}^{-1}) )</td>
<td></td>
</tr>
<tr>
<td>0.01</td>
<td>1.02 ± 0.02</td>
<td>1.02 ± 0.02</td>
<td>2.29</td>
<td>2.29</td>
</tr>
<tr>
<td>0.02</td>
<td>1.67 ± 0.10</td>
<td>0.84 ± 0.05</td>
<td>4.82</td>
<td>2.41</td>
</tr>
<tr>
<td>0.03</td>
<td>2.77 ± 0.15</td>
<td>0.92 ± 0.05</td>
<td>6.31</td>
<td>2.10</td>
</tr>
<tr>
<td>0.04</td>
<td>3.71 ± 0.12</td>
<td>0.93 ± 0.03</td>
<td>8.88</td>
<td>2.22</td>
</tr>
<tr>
<td>0.05</td>
<td>4.09 ± 0.14</td>
<td>0.82 ± 0.03</td>
<td>12.0</td>
<td>2.40</td>
</tr>
<tr>
<td>0.06</td>
<td>4.28 ± 0.11</td>
<td>0.72 ± 0.02</td>
<td>12.7</td>
<td>2.12</td>
</tr>
<tr>
<td>0.10</td>
<td>5.79 ± 0.08</td>
<td>0.58 ± 0.01</td>
<td>19.8</td>
<td>1.98</td>
</tr>
</tbody>
</table>

*At 40°C taken from ref. 21
yield the products (Eq. 3). When p-NO₂C₆H₄SMe is used as the substrate, an initial increase in the absorbance at 540 nm is noted which is an evidence for complex formation between the substrate and oxidant not via sulphur but through nitro group. Similar increase in absorbance has already been noted in the reaction of Cr(V) complex with NO₂⁻.

At high [sulphide] a limiting rate is observed due to saturation of intermediate I with substrate. Further increase in [sulphide] only changes its bulk concentration without affecting the rate of oxidation. It is interesting to recall that Cr(VI) oxidation of ArSMe followed simple second order kinetics, first order each in the oxidant and substrate, excluding any complex formation between Cr(VI) and sulphide (Table 1). The kinetic evidence for complex formation between Cr(V) and the substrate is obtained from the linear Michaelis-Menten plot. When 1/k₁ was plotted against 1/[MPS] the plot was linear with finite intercept indicating that the reactions follow the Michaelis-Menten kinetics (Fig. 1). The equilibrium or formation constant, K, of the complex can be evaluated from the above plot and the values of K for MPS, p-

MeC₆H₄SMe and p-OMeC₆H₄SMe are 7.7, 50 and 683 M⁻¹ respectively. Though we get a K value of 683 M⁻¹ for p-OMeC₆H₄SMe from the Michaelis-Menten plot we did not get spectral evidence for the formation of this complex. Similar weak complex formation between Cr(V) and thiolactic acid through sulphur has also been postulated.

It has been established that Cr(V) complex of HEBA is highly stable in the pH range of 3-4.5 (ref. 15). To check the stability of the complex under our experimental conditions (pH = 2) the rate of disproportionation of the complex in the absence of substrate at 540 nm is followed and the k₁ value for the self decomposition of this complex is 0.2 x 10⁻⁴ S⁻¹ and this value has been subtracted from the k₁ observed in the present study.

The reaction is catalyzed by [H⁺] and the increase in [H⁺] increases the rate of the reaction enormously (Table 3) and the order in H⁺, estimated from the plot of log k₁ versus log[H⁺], is found to be 0.75. It is pertinent to point out that similar catalytic role of H⁺ has also been observed in Cr(VI) oxidation of sulphides. The reaction is also profoundly influenced by the change in solvent composition. The increase in acetonitrile content of the medium increases the rate (Table 3), i.e., the decrease in polarity of the solvent facilitates the reaction as was found in the Cr(VI) oxidation of organic sulphides. A plot of log k₁ versus 1/D is fairly linear with a negative slope pointing to an interaction between a negative ion and a dipole. The observed solvent effect is in favour of an electron transfer process in the rate-determining step. As the increase in acetonitrile content of the
medium decreases the viscosity and dielectric constant of the medium, the formation of encounter complex is more facile thereby increasing the rate of electron transfer. As the rate of this reaction is not retarded by the added monomer, acrylonitrile and the redox system does not initiate polymerization, the formation of radical intermediates in the rate-controlling step is unlikely. The effect of altering ionic strength on the rate of the reaction is investigated by adding sodium perchlorate and the rate of the reaction is little affected by the change in ionic strength of medium which indicates the participation of a neutral molecule in the rate determining step.

To gain an insight into the mechanism of the reaction, the influence of introducing electron-releasing and electron-withdrawing substituents in the para-position of the phenyl ring of PhSMe on the rate of oxidation has been investigated at four different temperatures and the rate constant data are collected in Table 4. To our surprise, both electron-releasing groups like p-methyl and p-methoxy and electron-withdrawing p-chloro accelerate the rate of the reaction, though p-nitro group has profound retarding effect. The p-COOH group has rate constant value close to that of the parent compound. These results are in striking contrast to those of Cr(VI) oxidation of organic sulphides\(^2\) where electron-releasing groups accelerate the rate and all electron-withdrawing groups retard the rate of oxidation (Table 4). Though the kinetic data of para-substituted phenyl methyl sulphides are not in accordance with the polar effect of the substituents, the Hammett plot of \(k_1\) versus \(\sigma\) has been attempted for the three substrates \(\text{C}_6\text{H}_5\text{SMe}\), \(p\)-MeC\(_6\)H\(_5\)SMe and \(p\)-MeOC\(_6\)H\(_5\)SMe and the plot is linear \((r=0.994)\) giving the \(\rho\) value of \(-5.95\) at 293 K. The \(\rho\) value is highly sensitive to the temperature and the \(\rho\) values at 296 and 308 K are \(-4.49\) \((r=0.997)\) and \(-1.19\) \((r=0.982)\) respectively. At 313 K, the \(k_1\) values for these three substrates are very close and the correlation between \(\log k_1\) and \(\sigma\) is poor. If we include the sulphides containing electron-withdrawing groups also the Hammett plot is convex upwards which is explained later. The \(\rho\) value for the uncatalyzed Cr(V) oxidation of ArSMe in 50% aqueous acetonitrile is \(-1.80\). Though we cannot depend much on the \(\rho\) value obtained from the small number of data to decide the mechanism of oxidation\(^{22}\), the \(\rho\) value, particularly at 293 and 296 K, is high for Cr(V) oxidation compared to Cr(VI) oxidation under similar conditions. In the Ce(IV) oxidation of organic sulphides an electron transfer in the rate determining step has been proposed though the \(\rho\) value \((-3.3)\) is comparatively high\(^7\). Though the magnitude of \(\rho\) value cannot be taken as a conclusive evidence in favour of a mechanism, the difference in the \(\rho\) values and order in the substrate indicates that different mechanisms are operating in Cr(VI) and Cr(V) oxidations. Recently Naruta et al.\(^{23}\) have observed almost same rate constant for p-methyl and p-nitro phenyl methyl sulphides in the iodosylbenzene oxidation of aromatic sulphides catalyzed by iron complexes of chiral 'twin coronet' porphyrins. The authors have taken these results

| Table 3—Effect of varying \([H^+]\) and percentage of solvent composition on Cr(V) oxidation of MPS |
|---|---|---|---|
| \([H^+]\) M | \(k_1 \times 10^4 \text{ (s}^{-1})\) CH\(_3\)CN-H\(_2\)O | \(k_1 \times 10^4 \text{ (s}^{-1})\) % (v/v) |
| 0.001 | 0.58 ± 0.09 | 25-75 | 0.94 ± 0.08 |
| 0.005 | 0.84 ± 0.04 | 50-50 | 1.02 ± 0.02 |
| 0.01 | 1.20 ± 0.02 | 60-40 | 3.34 ± 0.42 |
| 0.04 | 4.37 ± 1.29 | 75-25 | 4.75 ± 0.52 |
| 0.10 | 18.9 ± 1.10 | 80-20 | 6.60 ± 0.89 |

\(^1\) solvent = 50% aqueous acetonitrile; \([H^+] = 0.01 \text{ M}\)

| Table 4—Pseudo-first order rate constants for \(p\)-\(\text{XCH}_6\text{H}_5\text{SMe}\) at four temperatures and \(\Delta H^r\) and \(\Delta S^r\) values |
|---|---|---|---|
| \(x\) | \(k_1 \times 10^4 \text{ (s}^{-1})\) 293 | 296 | 308 | 313 K |
| \(\Delta H^r\) (kJ mol\(^{-1}\)) | \(\Delta S^r\) (J mol\(^{-1}\) K\(^{-1}\)) | \(\Delta G^r\) (kJ mol\(^{-1}\)) |
| \(p\)-NO\(_2\) | 0.20 ± 0.03 | 0.45 ± 0.02 | 0.64 ± 0.07 | 0.79 ± 0.05 (0.01) | 51.0 | -160 | 99.5 |
| \(p\)-H | 0.40 ± 0.01 | 1.02 ± 0.02 | 8.24 ± 1.26 | 12.8 ± 0.87 (0.24) | 129 | +112 | 95.1 |
| \(p\)-Cl | 2.94 ± 0.34 | 4.82 ± 0.54 | 12.4 ± 0.46 | 18.6 ± 1.31 (0.10) | 64.7 | -90.7 | 92.2 |
| \(p\)-OMe | 15.1 ± 2.17 | 16.1 ± 1.68 | 17.6 ± 2.03 | 19.2 ± 0.52 (1.02) | 5.71 | -279 | 90.2 |
| \(p\)-COOH | 0.40 ± 0.07 | 2.62 ± 0.30 | 7.31 ± 0.51 | 9.84 ± 0.16 | 102 | +25.8 | 94.2 |
| \(p\)-Me | 5.70 ± 0.09 | 7.08 ± 0.79 | 11.7 ± 0.85 | 14.2 ± 0.32 (0.56) | 31.4 | -200 | 92.0 |

\(^{a}\)At 303 K

Values given in parentheses are for Cr(VI) oxidation under similar conditions, taken from ref: 21.
as an evidence for an electron transfer from the substrate to the oxidant in the rate-determining step. The data in Table 4 indicate that though p-CIC₆H₄SMe and p-MeOC₆H₄SMe have highly different k₁ values at 293 K, almost equal k₁ values have been observed at 313 K. Thus the interesting substituent effect observed tempted the authors to conclude that one electron transfer mechanism is operating for the parent, p-Me, p-MeO, p-Cl and p-COOH phenyl methyl sulphides and a different mechanism for p-NO₂C₆H₄SMe. However, the high p values (−5.95 and 4.49) and the absence of spectral evidence for Cr(IV) formation during the reaction are against the one electron transfer mechanism. A smaller p value has been observed in the oxoruthenium(IV) oxidation of ArSMe where a single electron transfer from sulphide to metal complex has been postulated.

Comparing the k₁ values of C₆H₄SMe, p-CIC₆H₄SMe and p-MeOC₆H₄SMe at 293 K with the corresponding values at 313 K, one can notice an interesting trend. Though the k₁ values for MPS and p-CIC₆H₄SMe are very small compared to that of p-OMeC₆H₄SMe at 293 K, the values are very close at 313 K. From the ΔH¹ and ΔS¹ data given in Table 4, we estimated the isokinetic temperature, β, from the isokinetic plot of ΔH¹ versus ΔS¹ (p-NO₂C₆H₄SMe is excluded as different mechanism is proposed for this substrate vide infra). The plot was linear (r=0.999) and the β value was found to be 314 K. As the isokinetic temperature is very close to the experimental temperature, all substituted phenyl methyl sulphides have very close k₁ values at 313 K. Thus the peculiar substituent effect may be attributed to the reaction being carried out at a temperature close to the isokinetic temperature of the reaction. The linear relationship between ΔH¹ and ΔS¹ suggests the operation of a similar mechanism in the parent and substituted phenyl methyl sulphides. Though the reactivity of sulphides is in accordance with the ΔG¹ values given in Table 4, the positive ΔS¹ values observed in the case of PhSMMe and p-CO₂H₆C₆H₄SMe indicate the difficulty in the formation of the transition state.

Mechanism and rate law

The observed kinetic results and arguments presented above suggest the reversible formation of a 1:1 complex between the oxidant and substrate (Eq. 2). Though we tried to observe spectral evidence for the formation of the complex II, we could not succeed. However the linear Michaelis-Menten plot with a finite intercept obtained can be taken as the kinetic evidence for the formation of complex II. Thus the observed kinetics can be accounted for in terms of a mechanism given in Eqs (2) and (3).

The steps (2) and (3) would lead to the rate law, Eq. (4).

\[
\frac{d[Cr(IV)]}{dt} = \frac{Kk[Cr(IV)][ArSMe]}{1 + K[ArSMe]}
\]

Rearrangement of Eq. (4) leads to Eq. (5) for the pseudo-first order rate constant, k₁

\[
\frac{d[Cr(IV)]}{dt} \times \frac{1}{[Cr(IV)]} = k₁ = \frac{Kk[ArSMe]}{1 + K[ArSMe]}
\]

Taking the reciprocal of Eq. (5) leads to Eq. (6)

\[
\frac{1}{k₁} = \frac{1}{Kk[ArSMe]} + \frac{1}{K[ArSMe]}
\]

which will result in a linear Michaelis-Menten plot of 1/k₁ versus 1/[ArSMe]. The values of K have been evaluated from the slope and intercept of 1/k₁ versus 1/[ArSMe] plot and the values for the C₆H₄SMe, p-MeC₆H₄SMe and p-OMeC₆H₄SMe respectively are K=7.7, 50 and 638 M⁻¹. The rate constant for the decomposition of the complex II, k, has been calculated from the intercept of the Michaelis-Menten plot and k values for C₆H₄SMe, p-MeC₆H₄SMe and p-OMeC₆H₄SMe are 1.41, 2.07 and 2.10 x 10⁻³ s⁻¹ respectively. The inference from the values of K and k obtained from the Michaelis-Menten plot is that though K is highly sensitive to the nature of substituent in C₆H₄SMe, k remains almost constant for all sulphides. Thus the formation of Cr(IV)-sulphide complex is rate determining and decomposition of the complex to yield products occurs by similar rate. We analysed the K values of C₆H₄SMe, p-MeC₆H₄SMe and p-OMeC₆H₄SMe with Hammett and Brown-Okamoto equations. Though the correlation for the plot of log K with Hammett σ is only satisfactory (r=0.970, ρ=−6.96), it is excellent with σ⁺ values (r=0.999, ρ=−2.49). Thus the higher K values in the case of sulphides containing electron-releasing groups like p-Me and p-OMe also support the postulation of complex formation between Cr(IV) and sulphide. The formation of Cr(IV)-sulphide complex II and the products ArSOMe and Cr(III) due to ligand coupling between the O and sulphur in II can be represented as in Scheme 1.
The formation of $S-Cr$ bond is facilitated by electron-releasing groups in the $\text{para}$-position of phenyl ring. However, ligand coupling between $S$ and $O^-$ will be more favourable if $S$ is more electron deficient which is achieved by electron-withdrawing groups in the phenyl ring of PhSMe. Thus the observed substituent effect at temperatures far from isokinetic temperature can be accounted for in terms of the mechanism shown in Scheme 1. However substituent effect is minimum at the temperature close to $\beta$. Ligand coupling reactions have been postulated recently by us in the catalyzed Cr(VI) oxidation of organic sulphides and by many other workers. The formation constant, $K$, for the Cr(V)-thioether complex may increase with increase in $[\text{H}^+]$ thereby increasing the rate of oxidation. A similar increase in the rate of the Cr(VI)-thioester complex with increasing $[\text{H}^+]$ has been postulated by Bose et al. and Connett and Wetterhahn for the oxidation of thiols. Further the protonation of Cr(V) complex makes the oxidant more electrophilic (Eq. 7) thereby favouring the nucleophilic attack of sulphides on chromium at high $[\text{H}^+]$. Thus the profound acid catalysis of the reaction also supports this mechanism. It is to be pointed out that at each $[\text{H}^+]$, the self decomposition of Cr(V) complex has been taken into account in the measurement of $k_1$ for the Cr(V) oxidation of sulphide.

It is worthwhile to compare this mechanism with the mechanism postulated recently for the oxochromium(V)-salen complex oxidation of alkyl aryl sulphides. SalenH$_2$ is a schiff base prepared from ethylenediamine and salicylaldehyde. This oxidation reaction followed simple second order kinetics, first order each in the oxidant and substrate. Further the reaction is accelerated by electron-releasing groups and retarded by electron-withdrawing substituents in the phenyl ring of PhSMe. To account for the kinetic results, the nucleophilic attack of sulphide at the chromium of the oxochromium(V) complex in the rate determining step followed by fast ligand coupling of sulphide and $O^-$ in the hypervalent intermediate to form the sulphoxide and Cr(III) complex has been postulated. Thus the important aspect is that though both are Cr$^V=O$ oxidants, the mechanism of the oxidation reaction differs with change in the nature of the ligand. However, from the kinetic measurements we cannot distinguish electron transfer mechanism from the nucleophilic attack of sulphide at Cr(V).

The addition of $p$-NO$_2$C$_6$H$_4$SMe to Cr(V) is accompanied by an initial increase in absorbance at 540 nm. This observation indicates the formation of a precursor complex between sulphide and Cr(V), probably through the oxygen end of $O=Cr(V)$. A similar increase in absorbance at 510 nm with the addition of nitrite ion to Cr(V) has been observed by Rajavelu and Srinivasan (This difference in $A_{\text{max}}$ is the result of difference in the solvent system). Thus a different mechanism is operating in the Cr(V) oxidation of $p$-NO$_2$C$_6$H$_4$SMe. The different behaviour of $p$-NO$_2$C$_6$H$_4$SMe towards the oxidant from other sulphides will be studied in detail and reported separately.

Comparison with the Cr(VI) oxidation of organic sulphides

The kinetics of Cr(VI) oxidation of aryl methyl sulphides have been studied in aqueous acetic acid and in aqueous acetonitrile and the results in both media are very similar. For comparison, the $k_1$ and $k_2$ values obtained for Cr(VI) oxidation of C$_6$H$_5$SMe in aqueous acetonitrile are given in Table 1 and for substituted phenyl methyl sulphides in Table 4. The $k_1$ values for Cr(V) oxidation of ArSMe are 20-180 times more than $k_1$ values of Cr(VI) oxidation under similar conditions. Though both oxidation reactions are first order in the oxidant, the order in the substrate is different, first order in Cr(VI) oxidation and fractional order in Cr(V) oxidation. The acid and solvent dependence are analogous in both oxidations. However, the substituent effect is different. Though all electron-releasing groups accelerate and electron-withdrawing groups retard the rate of Cr(VI) oxidation, electron-withdrawing groups like $p$-Cl and $p$-
COOH behave differently in Cr(V) oxidation. There is no kinetic evidence for complex formation between the oxidant and substrate in Cr(VI) oxidation but the linear Michaelis-Menten plot with finite intercept supports the formation of complex between Cr(V) and sulphides. The plot of log $k_1$ versus the oxidation/ionization potentials of ArSMe was excellently linear in the Cr(VI) oxidation of organic sulphides indicating single electron transfer in the rate determining step. Such a correlation cannot be attempted in the present study as both electron-releasing and some electron-withdrawing groups present in the para-position of phenyl ring accelerate the reaction. Thus the different kinetic results observed indicate the operation of different mechanisms in the Cr(VI) and Cr(V) oxidation of organic sulphides.

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References