Spectral Evidence for the One-Step Three-Electron Oxidation of Phenylsufinylacetic Acid and Oxalic Acid by Cr(VI)

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Received June 23, 2013; revised July 25, 2013; accepted August 20, 2013

ABSTRACT

The co-oxidation of a mixture of phenylsulfinylacetic acid (PSAA) and oxalic acid (OxH2) by Cr(VI) in 20% acetonitrile-80% water (v/v) medium follows third order kinetics, first order, each with respect to PSAA, OxH2 and Cr(VI). The reaction involves nucleophilic attack of sulfur atom of PSAA on chromium of the oxidizing species, Cr(VI)-OxH2 to form a ternary complex, Cr(VI)-OxH2-PSAA followed by a one-step three-electron reduction of Cr(VI) to Cr(III) and simultaneous oxidation of both the substrates. The reaction is catalysed by Mn2+ ion while retarded by Al3+ ion. Electron releasing substituents in the meta- and para-positions of the phenyl ring of PSAA enhance the rate of co-oxidation while electron withdrawing substituents retard the reaction. The Hammett plots at different temperatures exhibit excellent correlation with negative $\rho$ values. The reaction series obey isokinetic relationship and the observed isokinetic temperature is lying below the experimental range of temperature.

Keywords: Phenylsulfinylacetic Acid; Oxalic Acid; Co-Oxidation; Nucleophilic Attack of Sulfur; Three-Electron Transfer; Substituent Effect

1. Introduction

Oxalic acid acts as an efficient catalyst and enhances the rate of Cr(VI) oxidation of many inorganic [1-3] and organic compounds [4-10]. The oxalic acid catalysed processes involve the formation of Cr(IV)/Cr(V) intermediate species depending on the substrate, nature of Cr(VI) oxidizing reagent and experimental conditions. However, in the Cr(VI) co-oxidation of alcohol and oxalic acid, Rocek and co-workers [11] observed a direct reduction of Cr(VI) to Cr(III) without the formation of these intermediate species of chromium. In co-oxidation, oxalic acid undergoes oxidation in a stoichiometric ratio yielding CO2 along with the other reductants with tremendous rate acceleration. Such type of rate enhancement with oxalic acid by Cr(VI) is observed with diverse substrates like formic acid [12], aromatic anils [13], anilides [14], cycloalkanones [15] and cinnamic acids [16].

Since the co-oxidation process offers the possibility of several synthetic applications, Cr(VI) co-oxidation studies are of striking significance. Srinivasan et al. [17] reported the co-oxidation of phenylmethyl sulfoxides and oxalic acid with Cr(VI) and designed the mechanism for the reaction which also highlights the substituent effect. Das et al. [18] monitored the micellar effect on the co-oxidation of dimethyl sulfoxide and oxalic acid by Cr(VI) considering it as a probe for three-electron transfer in a single step. In the case of co-oxidation of S-phenylmercaptoacetic acid and oxalic acid with pyridinium chlorochromate [19], two different mechanisms, based on substrate concentration, have been suggested. The significant utility of phenylsulfinylacetic acid (PSAA) in various synthetic routes [20-26] prompted the present investigation. Detailed literature scanning also reveals that there is no systematic kinetic report on PSAA and so, the present study of Cr(VI) co-oxidation of PSAA with oxalic acid (OxH2) is undertaken and its salient features along with the substituent effects are discussed.

2. Experimental

The substrate, phenylsulfinylacetic acid and several meta-
and para-substituted PSAAs were synthesized from the corresponding phenylmercaptoacetic acids by controlled oxidation with $\text{H}_2\text{O}_2$ [27], recrystallised from suitable solvents and their melting points were checked with the literature values [28]. The purity was further verified by LCMS. Potassium dichromate (BDH), sodium perchlorate (BDH), perchloric acid (Merck), oxalic acid (Merck), aluminium nitrate (Merck) and all other reagents were of AnalaR grade and they were used as such for the preparation of solutions of desired concentration for the kinetic study using double distilled water. Literature procedures were adopted for the purification of solvents, acetonitrile and water.

2.1. Kinetic Measurements

The kinetic study was performed under pseudo-first order conditions by maintaining $\left(\text{PSAA}, \text{OxH}_2\right) >>> \text{[Cr(VI)]}$, in 20% acetonitrile-80% water mixture (v/v) and the progress of the reaction was observed by monitoring the decay of Cr(VI) at 351 nm at different time intervals with an ELICO Double Beam UV-vis Bio-spectrophotometer with an inbuilt thermostat. Figure 1 shows the spectral changes recorded during the reaction.

The pseudo-first order rate constant ($k_1$) for each kinetic run was evaluated from the slope of the linear plot of log OD vs time by the method of least squares. The second order rate constant ($k_2$) was calculated from the relation: $k_1 = k_2[\text{PSAA}]$. The precision of the k values is given in terms of 95% confidence limits of Students’ t test.

2.2. Product Analysis

To characterize the products of the reaction, the reaction mixture containing excess of Cr(VI) over PSAA and OxH$_2$ was kept for 48 hours for completion of the reaction and then extracted with ether. The ether extract was collected, dried over anhydrous sodium sulfate and the solvent was removed by evaporation. The residue obtained from the ether extract was dried and subjected to GC-MS (Figure 2) and LC-MS (Supplementary Material: Figure F1) analysis. The parent peak at $m/z = 156$ in GC-MS and the peak eluted in LC-MS at a retention time of 1.87 min ionizes in APCI (+) mode with an area of 86% corresponding to the mass 157 indicate that methyl-phenyl sulfone is the sole product formed. The presence of strong IR bands (Supplementary Material: Figure F2) at 1148 cm$^{-1}$ and 1290 cm$^{-1}$ characteristic of symmetric and asymmetric stretching respectively of $>\text{SO}_2$ group further supports the formation of the product, methyl-phenyl sulfone.

The final fate of chromium (VI) can be predicted from the UV-visible spectroscopy by scanning the aqueous extract of the product mixture and comparing the spectral changes observed with that of authentic sample of Cr(III). The two UV-vis peaks of Cr(III) at 421 nm and 592 nm (Figure 3(a)) which were assigned to its octahedral transitions, $^4A_{2g} \rightarrow ^4T_{1g}$ (F) and $^4A_{2g} \rightarrow ^4T_{2g}$ (F) [29,30] were found to shift to lower wavelength regions, 414 nm and 562 nm for the product mixture (Figure 3(b)). This observation clearly indicates the existence of chromium as Cr(III) in the form of complex species probably with oxalic acid as observed by other researchers [31,32] and not exist as free ion.

3. Results and Discussion

The order of the reaction with respect to Cr(VI) is unity under pseudo-first order conditions of $\text{[PSAA]}, \text{[OxH}_2]\gg \text{[Cr(VI)]}$ which is clear from the linear plots of logOD vs time even upto 75% completion of reaction and constant pseudo-first order rate constant values. However, it is observed that in the lower regions of [Cr(VI)], the pseudo-first order rate constant increases with decrease in [Cr(VI)].
the medium (Supplementary material: the medium from 10% to 80% acetonitrile shows an accelerating effect with decrease in dielectric constant of Mn$^{2+}$). The decrease in rate with increase in Cr(VI) in lower concentration region may be due to the dimerization of Cr(VI) followed by decrease in concentration of active species [33-35] or due to the existence of some sort of weak association between monomeric Cr(VI) species [36].

The reaction is first order each in PSAA and oxalic acid, which are evidenced from the constant values obtained by dividing $k_1$ by [PSAA] or [OxH$_2$] and also from the unit slope of their respective log-log plots of $k_1$ vs [PSAA] and [OxH$_2$]. The co-oxidation rate increases linearly with increase in $[\text{H}^+]$ (Supplementary material: Table T1) and shows a first order dependence with respect to [H$^+$]. This shows the protonation of Cr(VI) species in the experimental conditions which enhances the electrophilic activity of the oxidant. Solvent variation of the medium from 10% to 80% acetonitrile shows an accelerating effect with decrease in dielectric constant of the medium (Supplementary material: Table T1).

The effect of Mn$^{2+}$ on rate (Supplementary material: Table T2) indicates that the rate of co-oxidation increases linearly with increase in [Mn$^{2+}$] which is contrary to the retardation effect of Mn$^{2+}$ on Cr(VI) oxidation due to the removal of Cr(IV) intermediate by Mn$^{2+}$. The observed acceleration effect not only excludes the involvement of Cr(IV) intermediate in this reaction but also indicates that Mn$^{2+}$ acts as a catalyst. Such type of Mn$^{2+}$ catalysis during co-oxidation process is witnessed by several authors [14,15,17]. Suppression of rate by the addition of aluminium nitrate (Supplementary material: Table T2) may be visualized due to the removal of OxH$_2$ by Al$^{3+}$.

3.1. Substituent Effect

The effect of substituents on the rate of co-oxidation is examined with several meta- and para-substituted PSAAs at three different temperatures viz., 15°C, 20°C and 30°C. The second order rate constants and the activation parameters calculated from the Eyring’s plot are enumerated in Table 2. To have a better insight into the contribution of substituent effect on the rate and mechanism, the rate constants were correlated with Hamnett $\sigma$ constants and found that an excellent correlation is obtained with negative $\rho$ values (Supplementary material: Figure F3).

An analysis of the data in respect of linear free energy relationships reveals that the reaction series obeys isokinetic relationship as per the equation,

$$\Delta H^* = \Delta H_0 + \beta \Delta S^*$$

where, $\beta$ is the isokinetic temperature, at which all the substituents in a given series have the same reactivity.

The kinetic results revealed that the co-oxidation of Cr(VI) species in the reaction mixture depends mostly on the concentration of H$^+$ and Cr(VI). In aqueous acidic solution, the various possible forms of Cr(VI) species are H$_2$CrO$_4$, HCrO$_4^-$ and HCrO$_5^-$ [39,40]. The species, HCrO$_4^-$ exists only at very low concentration of H$^+$ [41] and hence under the maintained experimental conditions of H$^+$ the participation of HCrO$_4^-$ is excluded. At higher concentrations of H$^+$, the existence of Cr(VI) in the form HCrO$_5^-$ has been proved by several researchers [35,42,43] and on this basis its participation in the present co-oxidation process is envisaged. The positive slope obtained from the linear plot of log$k_1$ vs 1/D along with first order dependence on [H$^+$] supplement the involvement of a positively charged Cr(VI) species in the rate determining step.

The kinetic results revealed that the co-oxidation of phenylsulfinylacetic acid and oxalic acid by Cr(VI) follows the rate law,

$$-d[\text{Cr(VI)}]/dt = k[\text{PSAA}][\text{OxH}_2][\text{H}^+][\text{Cr(VI)}]$$
Table 1. Rate constants for the co-oxidation of PSAA and OxH₂ by Cr(VI).

<table>
<thead>
<tr>
<th>[PSAA] (mol·dm⁻³)</th>
<th>10⁴ k₁ (s⁻¹·g⁻¹)</th>
<th>10⁴ [Cr(VI)] (mol·dm⁻³)</th>
<th>10⁴ k₁ (s⁻¹)</th>
<th>10⁴ [OxH₂] (mol·dm⁻³)</th>
<th>10⁴ k₁ (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.65 ± 0.07</td>
<td>0.5</td>
<td>32.7 ± 1.51</td>
<td>0</td>
<td>1.46 ± 0.04</td>
</tr>
<tr>
<td>0.8</td>
<td>2.76 ± 0.08</td>
<td>1.0</td>
<td>18.5 ± 0.37</td>
<td>1.0</td>
<td>3.22 ± 0.13</td>
</tr>
<tr>
<td>2.0</td>
<td>7.11 ± 0.23</td>
<td>2.0</td>
<td>15.8 ± 0.88</td>
<td>2.0</td>
<td>5.36 ± 0.26</td>
</tr>
<tr>
<td>3.0</td>
<td>10.4 ± 0.37</td>
<td>3.0</td>
<td>10.4 ± 0.37</td>
<td>3.0</td>
<td>7.52 ± 0.21</td>
</tr>
<tr>
<td>5.0</td>
<td>15.1 ± 0.34</td>
<td>4.0</td>
<td>11.8 ± 0.31</td>
<td>5.0</td>
<td>12.6 ± 0.24</td>
</tr>
<tr>
<td>9.0</td>
<td>27.2 ± 0.86</td>
<td>5.0</td>
<td>10.6 ± 0.54</td>
<td>7.0</td>
<td>18.8 ± 0.50</td>
</tr>
<tr>
<td>10</td>
<td>35.2 ± 0.98</td>
<td>6.0</td>
<td>11.3 ± 0.24</td>
<td>8.0</td>
<td>21.1 ± 0.64</td>
</tr>
<tr>
<td>20</td>
<td>60.6 ± 1.62</td>
<td>9.0</td>
<td>23.3 ± 1.20</td>
<td>25.1 ± 0.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>28</td>
<td>80.1 ± 3.00</td>
</tr>
</tbody>
</table>

[Cr(VI)] = 3.0 × 10⁻⁴ mol·dm⁻³; [OxH₂] = 1.0 × 10⁻² mol·dm⁻³; [H⁺] = 0.75 mol·dm⁻³; 1 = 0.8 mol·dm⁻³; solvent = 20% CH₃ CN-80% H₂O (v/v); [PSAA] = 3.0 × 10⁻² mol·dm⁻³.

Table 2. Second-order rate constants, enthalpy and entropy of activations for the co-oxidation of X-C₆H₄SOCH₂COOH and OxH₂ by Cr(VI).

<table>
<thead>
<tr>
<th>X</th>
<th>10⁴ k₂ (mol⁻¹·dm⁻¹·s⁻¹)</th>
<th>20°C</th>
<th>30°C</th>
<th>35°C</th>
<th>ΔH° (kJ·mol⁻¹)</th>
<th>ΔS° (JK⁻¹·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-Br</td>
<td>0.98 ± 0.03</td>
<td>1.63 ± 0.06</td>
<td>1.96 ± 0.07</td>
<td>33.5 ± 3.4</td>
<td>169 ± 12</td>
<td></td>
</tr>
<tr>
<td>m-Cl</td>
<td>1.14 ± 0.03</td>
<td>1.97 ± 0.02</td>
<td>2.29 ± 0.05</td>
<td>33.6 ± 1.9</td>
<td>167 ± 6.8</td>
<td></td>
</tr>
<tr>
<td>m-F</td>
<td>1.24 ± 0.03</td>
<td>2.11 ± 0.03</td>
<td>2.59 ± 0.14</td>
<td>35.2 ± 3.1</td>
<td>161 ± 11</td>
<td></td>
</tr>
<tr>
<td>p-Cl</td>
<td>1.57 ± 0.09</td>
<td>2.61 ± 0.07</td>
<td>3.17 ± 0.03</td>
<td>34.1 ± 3.1</td>
<td>163 ± 11</td>
<td></td>
</tr>
<tr>
<td>p-Br</td>
<td>1.36 ± 0.03</td>
<td>2.39 ± 0.01</td>
<td>2.85 ± 0.09</td>
<td>36.2 ± 1.8</td>
<td>157 ± 6.3</td>
<td></td>
</tr>
<tr>
<td>p-F</td>
<td>2.05 ± 0.07</td>
<td>3.23 ± 0.03</td>
<td>3.99 ± 0.18</td>
<td>31.7 ± 2.9</td>
<td>169 ± 10</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>2.47 ± 0.09</td>
<td>4.33 ± 0.08</td>
<td>5.05 ± 0.21</td>
<td>34.2 ± 3.7</td>
<td>159 ± 13</td>
<td></td>
</tr>
<tr>
<td>m-CH₃</td>
<td>2.69 ± 0.09</td>
<td>4.36 ± 0.04</td>
<td>5.39 ± 0.21</td>
<td>33.3 ± 2.7</td>
<td>161 ± 9.5</td>
<td></td>
</tr>
<tr>
<td>p-CH₃</td>
<td>3.77 ± 0.16</td>
<td>5.72 ± 0.10</td>
<td>6.91 ± 0.15</td>
<td>28.6 ± 2.7</td>
<td>175 ± 9.5</td>
<td></td>
</tr>
<tr>
<td>p-OC₂H₅</td>
<td>4.03 ± 0.16</td>
<td>6.29 ± 0.20</td>
<td>7.53 ± 0.16</td>
<td>29.8 ± 3.1</td>
<td>170 ± 11</td>
<td></td>
</tr>
<tr>
<td>p-OCH₃</td>
<td>4.40 ± 0.29</td>
<td>6.58 ± 0.13</td>
<td>8.36 ± 0.21</td>
<td>30.0 ± 3.7</td>
<td>168 ± 13</td>
<td></td>
</tr>
<tr>
<td>ρ</td>
<td>−0.94 ± 0.03</td>
<td>−0.87 ± 0.03</td>
<td>−0.88 ± 0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>r</td>
<td>0.995</td>
<td>0.992</td>
<td>0.994</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[X-C₆H₄SOCH₂COOH] = 3.0 × 10⁻² mol·dm⁻³; [OxH₂] = 0.01 mol·dm⁻³; [Cr(VI)] = 3.0 × 10⁻⁴ mol·dm⁻³; [H⁺] = 0.75 mol·dm⁻³; 1 = 0.8 mol·dm⁻³; solvent = 40% CH₃ CN-60% H₂O (v/v).

It has been reported that in the well-documented Cr(VI) oxidation of several substrates in the presence of oxalic acid, the cyclic form of an intermediate formed between Cr(VI) and oxalic acid is assumed to be the oxidizing species. Such complex formation between the oxidant and oxalic acid is indispensable for co-oxidation to occur [17]. In the present case too, addition of oxalic acid to Cr(VI) leads to a substantial hyperchromic shift at 263 nm and 351 nm in the UV-vis spectra of Cr(VI) (Figure 4(b)) which indicates the involvement of Cr(VI) in complex formation. Based on the above facts, it has been proposed that HCrO₄⁻ forms a cyclic complex (C₁, Scheme I) with oxalic acid in the first step of the mechanism. The rate acceleration is almost cancelled by the
addition of Al$^{3+}$ ion which is a direct evidence for the difficulty in the formation of Cr(VI)-OxH$_2$ species as Al$^{3+}$ removes OxH$_2$. Further, broadening of the peak at 263 nm which merges with the peak at 351 nm (Figure 4(d)) is perceived during the addition of Al$^{3+}$ ion to the reaction mixture.

In order to comprehend the subsequent steps in the mechanism of co-oxidation and the binding nature of PSAA with the oxidizing species, the UV-vis spectrum was recorded for the reaction mixture. The change in the shape as well as broadening of the peak at 263 nm in the presence of PSAA (Figure 4(c)) clearly reveals the formation of a new species probably termolecular intermediate complex, C$_2$. The formation of this intermediate, (Cr(VI)-OxH$_2$-PSAA) as a result of nucleophilic attack of sulfur of PSAA on chromium atom of the Cr(VI)-OxH$_2$ complex is the rate determining step. The importance of this intermediate, C$_2$ during co-oxidation is known from the significant rate acceleration observed when both PSAA and OxH$_2$ co-exists than their individual rate constants with Cr(VI) under the same experimental conditions. The high negative entropy of activation for this co-oxidation system ($\Delta S^{\ddagger} = -158.88 \pm 12.8$ JK$^{-1}$·mol$^{-1}$) when compared to that of the reaction without oxalic acid ($\Delta S^{\ddagger} = -24.49 \pm 0.09$ JK$^{-1}$·mol$^{-1}$) suggests that there exists a highly ordered transition state in the rate determining step.

As a result of electron transfer from sulfur of PSAA to chromium, a positive charge is developed on the sulfur center of the complex C$_2$. The negative $\rho$ value observed in the substituent effect study also confirms the existence of this charged state.

![Scheme 1](image-url)
of sulfonium ion intermediate in the rate determining step. The presence of electron releasing groups in the PSAA increase the electron density on sulfur atom of PSAA which makes PSAA a more efficient nucleophile for binding with the positively charged oxidizing species, Cr(VI)-OxH$_2$. Besides, electron releasing substituents stabilize the intermediate, C$_2$ while electron withdrawing substituents in PSAA destabilize it. The rapid oxidation of PSAA-oxalic acid mixture by Cr(VI) supports that the reduction of Cr(VI) through a termolecular complex must be much more favourable and hence faster than their individual oxidation reactions.

The intermediate, C$_2$ then undergoes several fast steps including ligand coupling and decarboxylation from PSAA moiety leading to the formation of the products. During this process, Cr(VI) is directly reduced to Cr(III) by a one-step three-electron transfer which involves a two electron transfer from PSAA and a one electron transfer from oxalic acid. The direct evidence for the one-step three electron transfer, i.e., reduction of Cr(VI) to Cr(III) arises from the existence of isobestic point at $\lambda_{max}$ 540 nm (Figure 1) in the overlay of the reaction mixture.

The involvement of OxH$_2$ as co-reductant and not as a catalyst in the reaction can be arrived from the amount of CO$_2$ liberated from the reaction. The number of moles of CO$_2$ liberated in the reactions with and without oxalic acid is determined quantitatively by the method described by Crossno et al. [44]. In the present reaction it has been observed that the amount of CO$_2$ liberated is more than one mole and this shows that CO$_2$ is liberated from oxalic acid too besides PSAA. The CO$_2^*$ thus formed may then undergo further rapid oxidation with Cr(VI) producing CO$_2$ and Cr(V). Then, Cr(V) reacts with another molecule of PSAA forming products.

4. Conclusion

The co-oxidation of phenylsulfinylacetic acid and oxalic acid by Cr(VI) follows three electron transfer mechanisms. The reduction of Cr(VI) to Cr(III) in a concerted step is assumed to be effective by the active oxidising species, Cr(VI)-OxH$_2$ via a termolecular complex, Cr(VI)-OxH$_2$-PSAA. The product analysis is also in support of the proposed mechanism.

REFERENCES


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Supplementary Materials

Figure F1. LC-MS analysis of the product.

Figure F2. IR spectra of the product.

Figure F3. Hammett plot at 30°C.
Table T1. Effect of solvent composition, [H\(^+\)] and ionic strength on rate constant at 30°C.

<table>
<thead>
<tr>
<th>CH(_3)CN-H(_2)O (%, v/v)</th>
<th>(10^4 k_1^{a}) (s(^{-1}))</th>
<th>(10^1 [H^+]) (mol dm(^{-3}))</th>
<th>(10^4 k_1^{b}) (s(^{-1}))</th>
<th>I (mol dm(^{-3}))</th>
<th>(10^6 k_1^{c}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 – 90</td>
<td>9.43 ± 0.22</td>
<td>2.5</td>
<td>3.42 ± 0.10</td>
<td>0.8</td>
<td>10.4 ± 0.37</td>
</tr>
<tr>
<td>20 – 80</td>
<td>10.4 ± 0.37</td>
<td>5.0</td>
<td>6.70 ± 0.15</td>
<td>1.0</td>
<td>10.3 ± 0.21</td>
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<tr>
<td>30 – 70</td>
<td>11.9 ± 0.25</td>
<td>7.5</td>
<td>10.6 ± 0.30</td>
<td>1.2</td>
<td>10.4 ± 0.34</td>
</tr>
<tr>
<td>40 – 60</td>
<td>13.0 ± 0.35</td>
<td>10.0</td>
<td>13.3 ± 0.20</td>
<td>1.4</td>
<td>10.7 ± 0.25</td>
</tr>
<tr>
<td>50 – 50</td>
<td>16.5 ± 0.23</td>
<td>12.5</td>
<td>16.7 ± 0.32</td>
<td>1.55</td>
<td>10.1 ± 0.26</td>
</tr>
<tr>
<td>60 – 40</td>
<td>20.2 ± 0.46</td>
<td>15.0</td>
<td>19.9 ± 0.44</td>
<td>1.8</td>
<td>11.2 ± 0.30</td>
</tr>
<tr>
<td>70 – 30</td>
<td>27.6 ± 0.89</td>
<td>20.0</td>
<td>32.5 ± 1.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80 – 20</td>
<td>40.8 ± 1.30</td>
<td></td>
<td></td>
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</tbody>
</table>

\([\text{Cr(VI)}] = 3.0 \times 10^{-4}\) mol dm\(^{-3}\); [PSAA] = \(3.0 \times 10^{-2}\) mol dm\(^{-3}\); \(4^a[H^+] = 7.5 \times 10^{-1}\) mol dm\(^{-3}\); \(4^bI = 0.8\) mol dm\(^{-3}\); \(4^cI = 1.1\) mol dm\(^{-3}\); solvent = 20% CH\(_3\)CN-80% H\(_2\)O (v/v).

Table T2. Effect of Mn\(^{2+}\) ion and Al\(^{3+}\) ion on reaction rate.

<table>
<thead>
<tr>
<th>(10^1 [\text{Mn}^{2+}]) (mol dm(^{-3}))</th>
<th>(^a10^4 k_1) (s(^{-1}))</th>
<th>(10^1 [\text{Al}^{3+}]) (mol dm(^{-3}))</th>
<th>(^b10^4 k_1) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10.3 ± 0.21</td>
<td>0</td>
<td>10.4 ± 0.37</td>
</tr>
<tr>
<td>1.0</td>
<td>11.9 ± 0.36</td>
<td>0.05</td>
<td>9.43 ± 0.21</td>
</tr>
<tr>
<td>2.0</td>
<td>13.9 ± 0.45</td>
<td>0.1</td>
<td>8.58 ± 0.33</td>
</tr>
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<td>5.0</td>
<td>19.4 ± 0.59</td>
<td>0.2</td>
<td>5.73 ± 0.25</td>
</tr>
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<td>7.0</td>
<td>27.6 ± 0.89</td>
<td>0.3</td>
<td>3.24 ± 0.15</td>
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<td>9.0</td>
<td>41.0 ± 1.50</td>
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<tr>
<td>10</td>
<td>44.9 ± 1.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\([\text{Cr(VI)}] = 3.0 \times 10^{-4}\) mol dm\(^{-3}\); [PSAA] = \(3.0 \times 10^{-2}\) mol dm\(^{-3}\); [OxH\(_2\)] = \(1.0 \times 10^{-2}\) mol dm\(^{-3}\); \(4^a[I] = 1.0\) mol dm\(^{-3}\); \(4^b[I] = 2.55\) mol dm\(^{-3}\).
Spectral and Mechanistic Investigation of Oxidative Decarboxylation of Phenylsulfinylacetic Acid by Cr(VI)

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(Received September 3, 2013; Accepted January 16, 2014)

ABSTRACT. The oxidative decarboxylation of phenylsulfinylacetic acid (PSAA) by Cr(VI) in 20% acetonitrile – 80% water (v/v) medium follows overall second order kinetics, first order each with respect to [PSAA] and [Cr(VI)] at constant [H⁺] and ionic strength. The reaction is acid catalysed, the order with respect to [H⁺] is unity and the active oxidizing species is found to be HCrO₃⁺. The reaction mechanism involves the rate determining nucleophilic attack of sulfur atom of PSAA on chromium of HCrO₃⁺ forming a sulfonium ion intermediate. The intermediate then undergoes α,β-cleavage leading to the liberation of CO₂. The product of the reaction is found to be methyl phenyl sulfone. The operation of substituent effect shows that PSAA containing electron-releasing groups in the meta- and para-positions accelerate the reaction rate while electron withdrawing groups retard the rate. An excellent correlation is found to exist between log k₂ and Hammett σ constants with a negative value of reaction constant. The ρ value decreases with increase in temperature evidencing the high reactivity and low selectivity in the case of substituted PSAAs.

Key words: Phenylsulfinylacetic acid, Oxidative decarboxylation, Nucleophilic attack of sulfur, Substituent effect

INTRODUCTION

Despite the vast usage of Cr(VI) for analytical and synthetic purposes,¹⁻³ it is well known for its carcinogenic and mutagenic activity.⁴⁻⁶ Though Cr(VI) is not directly responsible for DNA lesions, its tetrahedral conformation enables its active transport into the cell and generates highly reactive Cr(V), Cr(IV) and free radical intermediates by intracellular reduction capable of damaging DNA.⁷⁻⁹ Several researchers reported the mechanism of DNA damage induced by Cr(VI), but the crucial facets of this mechanism remain essentially unknown. Hence, the mechanistic aspects of reduction of Cr(VI) are of biologically important.

Organic sulfur compounds are model biological reductants. Realizing the biological importance of the interaction between sulfur and chromium, Cr(VI) oxidation of many organic sulfur compounds have been examined.¹⁰⁻¹³ Depending on the substrate and experimental conditions, different mechanistic pathways have been envisaged for Cr(VI) oxidation reactions: one electron transfer mechanism involving the formation of a cation radical intermediate in the slow step;¹⁴,¹⁵ a two electron transfer mechanism leading to the formation of Cr(IV) intermediate;¹⁶ the mechanism involving the formation of a chromate thioester¹⁷ and its disproportionation in a slow step;¹⁸ the Sₐ₂ mechanism involving a nucleophilic attack of sulfur on chromium followed by ligand coupling between S and O;¹⁵,¹⁹,²⁰ the mechanism which follows Michales-Menten kinetics with complex formation²¹ and slow decomposition of the complex.²² The present study of oxidative decarboxylation of phenylsulfinylacetic acid (PSAA) by Cr(VI) will be of particular interest owing to the application of PSAA in pharmaceutical preparations and in the synthesis of several organic compounds.²³⁻²⁹ The literature survey also reveals that there is no systematic report on the kinetic and mechanistic aspects on the oxidation of phenylsulfinylacetic acid except our recent report and hence the title investigation was undertaken to analyze the salient features of the reaction, the effect of substituents on the reaction rate and to arrive at a suitable mechanism.

EXPERIMENTAL

Materials

Phenylsulfinylacetic acid and several para- and meta-substituted phenylsulfinylacetic acids were prepared from the corresponding phenylmercaptoacetic acids by controlled oxidation using equimolar quantity of H₂O₂ and recrystallised from suitable solvents.³² The recrystallised phe-
Perumal Subramaniam, Natesan Thamizh Selvi, and Soundarapandian Sugirtha Devi

Nylsulfinylacetic acids were dried, melting points were determined and checked with the literature values. The purity was also ascertained by LC-MS for all the phenylsulfinylacetic acids. Then they were stored in the vacuum desiccator and used for the kinetic studies. Phenylmercaptoacetic acids required for the synthesis of PSAAs were synthesized by condensing chloroacetic acid (4.7 g in 20 ml of 20% sodium hydroxide) with appropriate thiophenol (0.05 mole) dissolved in 10 ml of 20% sodium hydroxide at 120–130 °C for five hours. The phenylmercaptoacetic acids formed were recrystallised from water and their melting points were verified with the literature values.

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Potassium dichromate (Merck), sodium perchlorate (Merck), perchloric acid (Merck) and all other reagents used were of AnalaR grade. Solvents, acetonitrile and water were purified by established procedures.

**Kinetic Measurements**

The reactions were carried out under pseudo first order conditions by maintaining [PSAA] » [Cr(VI)] in 20% acetonitrile−80% water (v/v) medium. The progress of the reaction was followed, using Elico Double beam UV-vis Bio-spectrophotometer with an inbuilt thermostat, by monitoring the decrease in absorbance of Cr(VI) at the λ_{max} of 351 nm at definite time intervals.

The spectral changes at different time intervals during the course of the reaction are given in Fig. 1. The pseudo first order rate constant (k_{1}) for each kinetic run is evaluated from the slope of log OD vs time by the method of least squares. The second order rate constant (k_{2}) is calculated from the relation: k_{2} = k_{1}/[PSAA]. The precision of the k values is given in terms of 95% confidence limits of the student’s t test.

**Stoichiometry and Product Analysis**

The stoichiometry of the reaction was determined by taking different ratios of Cr(VI) and PSAA concentrations under the condition [Cr(VI)] » [PSAA]. The estimation of unreacted Cr(VI) in the reaction mixture after completion of the reaction showed that two moles of Cr(VI) reacted with three moles of the substrate.

The reaction mixture in the stoichiometric condition was kept for 48 hours to ensure completion of the reaction. The solvent was then evaporated and extracted with ether. The ether layer was collected, dried over anhydrous sodium sulfate and the ether was removed by evaporation. IR and GC-MS analysis (Supplementary material: Figures S1 and S2) of the residue obtained from the ether extract confirm that methyl phenyl sulfone is the only product of the reaction. IR spectrum shows strong bands at 1148 cm⁻¹ and 1290 cm⁻¹ characteristic of symmetric and asymmetric stretching frequencies respectively for >SO₂ group.

**RESULTS**

The UV-visible spectrum of Cr(III) ion shows two peaks at 410 nm and 580 nm which are attributed to the octahedral transitions, 4A_{2g}(F)→4T_{1g}(F) and 4A_{2g}(F)→4T_{2g}(F) of Cr(III) whereas that of the reaction mixture after completion of the reaction shows two peaks at 411 nm and 565 nm which confirms the existence of Cr(III) as the final product of Cr(VI). The observed blue shift in λ_{max} value at 580 nm for the product mixture clearly points out that the product Cr(III) exists not as a free state but in the form of complex with other species, probably with methyl phenyl sulfone.

The overlaid spectra of the reaction in the wavelength range 500–620 nm (Fig. 2) exhibit a delayed increase in OD which is consistent with the formation of Cr(III). The delayed increase in OD in the region 500–620 nm without any isobestic point clearly shows that there are two or more competing reactions involving Cr(III) in the final stage of the reaction.

Under the experimental condition, [PSAA] » [Cr(VI)], the reaction exhibits first order dependence on Cr(VI) as evidenced by the linear log OD vs time plots even beyond 70% completion of the reaction. However, the calculated pseudo first order rate constants decrease with the increase in Cr(VI) concentrations (Table 1). The reason for this decrease in reaction rate may be due to the dimerization of Cr(VI).

![Figure 1. UV-visible spectra for the kinetic run, [PSAA] = 5.0×10⁻² mol dm⁻³, [Cr(VI)] = 3.0×10⁻⁴ mol dm⁻³, [H⁺] = 0.75 mol dm⁻³.](image-url)
followed by decrease in concentration of active species at higher concentrations of Cr(VI). Karunakaran et al. revealed that the increase in [Cr(VI)] may lead to some sort of weak association among the monomers resulting decrease in reactivity.

A plot of log $k_1$ vs log [PSAA] is linear with unit slope (slope = $1.02 \pm 0.01$, $r = 0.999$) indicating that the order with respect to substrate is one. This is further confirmed by the constant second order rate constant values obtained at different initial concentrations of PSAA and the linear plot of $k_1$ against [PSAA] ($r = 0.999$) which passes through the origin.

The rate constants are found to increase appreciably with increase in the concentration of HClO₄(Supplementary material: Table S1). The reaction is first order with respect to hydrogen ion as evidenced from the unit slope of the plot of log $k_1$ vs log [H⁺] (slope = $0.985 \pm 0.04$, $r = 0.999$) and constant value obtained by dividing pseudo first order rate constant by [H⁺]. The rate dependence on H⁺ establishes the involvement of protonated chromium species in the reaction. The effect of altering ionic strength on the rate of the reaction was investigated by adding sodium perchlorate and there is a slight increase in the rate with the increase in ionic strength of the medium (Supplementary material: Table S1). This could be attributed to the participation of a neutral molecule as one of the reactants in the rate determining step.

The rate constant increases significantly with the increasing acetonitrile content of the medium (Supplementary material: Table S1) indicating a facile reactivity in the medium of low dielectric constant. The rate enhancement in low dielectric constant medium may be due to an increase in reduction potential of Cr(VI)/Cr(III) couple with increase in acetonitrile content in the medium. The plot of log $k_1$ vs 1/dielectric constant is linear ($r = 0.997$) with a positive slope which indicates that one of the reactants involved in the rate controlling step is cationic in nature.

### SUBSTITUENT EFFECT

As the study of influence of substituents on the rate of reaction often provides an insight into the nature of the transition state and mechanism, the rate constants for the oxidative decarboxylation of several meta- and para-substituted PSAAs are determined at three different temperatures, viz., 10 °C, 20 °C and 30 °C and the second order rate constants are listed in Table 2.

The study of substituent effect reveals that electron releasing substituents accelerate the reaction rate while electron withdrawing substituents retard it. The second order rate constants of meta- and para-substituted PSAAs correlate excellently with Hammett substituent constants, $\sigma$ with negative slope values (Fig. 3).

The negative reaction constants, $\rho$ support the generation of electron deficient sulfur center in the transition state. The second order rate constant values obtained at three different temperatures for the meta- and para-substituted PSAAs, are employed to get thermodynamic parameters, $\Delta^{r}H$ and $\Delta^{r}S$ from the slope and intercept values of Eyring’s plots and are enumerated in Table 2. The data collected in Table 2 shows that the change in substituents in the phenyl group of PSAA has no effect on the enthalpy of activation, ($\Delta^{r}H$).
Table 2. Second order rate constants, enthalpy and entropy of activation for the oxidative decarboxylation of $X\text{C}_6\text{H}_4\text{SOCH}_2\text{COOH}$

<table>
<thead>
<tr>
<th>$X$</th>
<th>10$^3$ $k_2$ ($\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$)</th>
<th>$\Delta^\text{H}$ ($\text{kJ mol}^{-1}$)</th>
<th>$-\Delta^\text{S}$ ($\text{JK}^{-1}\text{mol}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-Br</td>
<td>1.18 ± 0.08</td>
<td>73.55 ± 3.7</td>
<td>39.99 ± 13.4</td>
</tr>
<tr>
<td>m-Cl</td>
<td>1.25 ± 0.05</td>
<td>73.57 ± 2.8</td>
<td>40.02 ± 10.1</td>
</tr>
<tr>
<td>m-F</td>
<td>1.26 ± 0.07</td>
<td>79.08 ± 2.8</td>
<td>20.21 ± 10.2</td>
</tr>
<tr>
<td>p-Cl</td>
<td>1.77 ± 0.08</td>
<td>78.83 ± 3.2</td>
<td>18.57 ± 11.6</td>
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<tr>
<td>p-Br</td>
<td>2.06 ± 0.10</td>
<td>75.28 ± 2.9</td>
<td>29.88 ± 10.5</td>
</tr>
<tr>
<td>p-F</td>
<td>3.30 ± 0.08</td>
<td>68.47 ± 1.9</td>
<td>50.23 ± 7.21</td>
</tr>
<tr>
<td>H</td>
<td>3.50 ± 0.16</td>
<td>75.58 ± 2.5</td>
<td>24.49 ± 8.94</td>
</tr>
<tr>
<td>m-CH$_3$</td>
<td>5.19 ± 0.19</td>
<td>72.01 ± 2.8</td>
<td>33.98 ± 10.3</td>
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<tr>
<td>p-CH$_3$</td>
<td>7.18 ± 0.38</td>
<td>69.55 ± 3.9</td>
<td>39.56 ± 14.2</td>
</tr>
<tr>
<td>p-i-bu</td>
<td>7.99 ± 0.31</td>
<td>69.39 ± 4.0</td>
<td>39.19 ± 14.7</td>
</tr>
<tr>
<td>p-OC$_3$H$_5$</td>
<td>8.22 ± 0.26</td>
<td>67.63 ± 2.4</td>
<td>45.34 ± 8.68</td>
</tr>
<tr>
<td>p-OCH$_3$</td>
<td>10.5 ± 0.49</td>
<td>64.51 ± 3.9</td>
<td>54.31 ± 14.2</td>
</tr>
<tr>
<td>$\rho$</td>
<td>−1.42 ± 0.08</td>
<td>−1.25 ± 0.08</td>
<td>0.996</td>
</tr>
</tbody>
</table>

$[X\text{C}_6\text{H}_4\text{SOCH}_2\text{COOH}] = 3.0 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{Cr(VI)}] = 3.0 \times 10^{-4} \text{mol dm}^{-3}$, $[\text{H}] = 0.75 \text{mol dm}^{-3}$, $I = 0.8 \text{mol dm}^{-3}$; Solvent: 40% CH$_3$CN - 60% H$_2$O (v/v).

DISCUSSION

The data in Table 2 demonstrate that the reactivity of PSAs is altered significantly by changing the substituents in the meta- and para-positions of the phenyl ring of PSAA. Also within a given set of substituted PSAs, appreciable increase in reactivity is noted with increase in temperature i.e., the $\rho$ value decreases with increase in temperature. The high reactivity ($k_2$ value) and low selectivity ($\rho$ value) observed at high temperatures in the case of substituted PSAAs is somewhat unexpected. This is due to the reactivity-selectivity principle (RSP) is in operation in this system. Hence, an attempt has been made to analyse the data by applying the method formulated by Exner to verify the operation of RSP. Accordingly, the rate data reported in Table 2 is subjected to mathematical treatment using the following equations.

\[
\log k_{fi} = a + b \log k_{si} + \varepsilon_i \tag{1}
\]

\[
\Delta = \left( \sum_i \log k_{fi} - \sum_i \log k_{si} \right) / N \tag{2}
\]

where $k_{fi}$ and $k_{si}$ are the second order rate constants for the fast and slow reactions i.e., at high and low temperatures respectively. $\varepsilon_i$ is the error of the log $k_{fi}$ versus log $k_{si}$ correlation, N is the total number of data points and $\Delta$ is the mean difference.

A linear relationship between the enthalpies and entropies called the isokinetic relationship, $\Delta^\text{H} = \Delta^\text{H}_0 + \beta^\text{S}$, where $\beta$ is the isokinetic temperature, is valid only if the Petersen’s error criteria is satisfied i.e., for a valid relationship between $\Delta^\text{H}$ and $\Delta^\text{S}$, the range of observed $\Delta^\text{H}$ (\(\Delta^\text{H}_\text{max}\)) must exceed 2$\delta$ (\(\delta\) is the maximum possible error).

In the present series of reactions, although Petersen’s error criteria is satisfied the plot of $\Delta^\text{H}$ vs $\Delta^\text{S}$ gives only a fair correlation ($r = 0.934$). Hence, the Exner’s plot of $\log k_2$ (30 $^\circ$C) against $\log k_2$ (10 $^\circ$C) is made which gives an excellent correlation ($r = 0.994$). The isokinetic temperature calculated from Exner’s plot is 192.4 K, which is below the experimental temperature.

Figure 3. Hammett plot for the reactions of substituted PSAAs with Cr(VI) at 30 $^\circ$C. $[X\text{C}_6\text{H}_4\text{SOCH}_2\text{COOH}] = 3.0 \times 10^{-2} \text{mol dm}^{-3}$, $[\text{Cr(VI)}] = 3.0 \times 10^{-4} \text{mol dm}^{-3}$, $[\text{H}] = 0.75 \text{mol dm}^{-3}$, $I = 0.8 \text{mol dm}^{-3}$; Solvent: 40% CH$_3$CN - 60% H$_2$O (v/v).
In the present system, among the three possible combinations of one fast reaction and one slow reaction at three different temperatures with a series of PSAAs, two combinations viz., 30 °C vs 20 °C and 20 °C vs 10 °C meet at a point, Y_o, and produce a magic point. The linear correlations obtained using equation (1) is depicted in Fig. 4.

The values of b obtained from equation (1) and \( \Delta \) calculated from equation (2), for all the three possible combinations of one fast and one slow reaction, are summarized in Table 3. The existence of magic point which is situated on the side of higher reactivity and the observed values of b which are less than unity and not too small values of \( \Delta \) are indication for the operation of a strong RSP in the present system. Such type of evidences have been taken for a valid RSP in many cases of salen catalysed oxidation of organic sulfides and sulfoxides by Chellamani et al.\(^{52-55}\)

The active species involved in the reaction may be Cr(VI) itself or Cr(V) formed as a result of one electron transfer or Cr(IV) as a result of two electron transfer. The absence of absorption at 750 nm, where Cr(V) is the only absorbing species\(^{56}\) rules out Cr(V) as the active species. The insensitivity of rate on added radical scavenger, acrylamide, and Mn^{2+} ions, scavenger for Cr(IV) rule out the involvement of Cr(V) and Cr(IV) respectively as active species. Hence, the active species in this reaction is assumed to be Cr(VI) itself which exists in aqueous acidic solution in a variety of forms such as H_2CrO_4, HCrO_3^- and HCrO_4^- depending on the pH of the medium. At low concentrations of H^+ it was observed that Cr(VI) exists predominantly as the monomer, HCrO_4^-\(^{57,58}\) and at higher concentrations of H^+ it mainly exists as HCrO_3^-\(^{14,19,59}\). Under the present experimental condition of 0.75 mol dm\(^{-3}\) [H^+], HCrO_3^- is assumed to be the effective oxidizing species. The positive nature of the oxidizing species is also evident from the positive slope obtained from the dielectric constant studies. The first order dependence of the reaction rate on H^+ gives further evidence for the protonated species, HCrO_3^+.

As the concentration of Cr(VI) is increased, progressively a smaller portion of the HCrO_3^+ is transformed into Cr_2O_7^{2-} and protonated forms according to the equilibrium (3) and these dimeric forms are the predominant species at concentrations greater than 0.05 M.\(^{19,60}\) As Cr_2O_7^{2-} and its protonated forms are poor electrophiles as compared to HCrO_3^+, this may be the reason for the decrease in rate constants with increasing Cr(VI) concentration.

\[
2\text{HCr}_2\text{O}_7\text{O}_3^- + \text{H}_2\text{O} \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + 4\text{H}^+ \quad (3)
\]

The spectral change observed in the region of \( \lambda_{\text{max}} \) between 230 and 270 nm becomes more important for the mechanistic study of Cr(VI) and sulfur compounds as it gives direct evidence for the existence of bond between chromium and sulfur.\(^{61-63}\) The time-dependent UV-visible spectrum of the reaction (Fig. 1) shows two equally intense absorption bands at 237 nm and 262 nm which have decreasing intensity with time. The decrease in intensity of absorption in this region with time may be due to the weakening of Cr(VI)–S bond as a result of decrease in concentration of PSAA and Cr(VI). The change in the absorption spectra of Cr(VI) with PSAA, the significant hyperchromic shift and the widening of the peak in the region 200–300 nm for the reaction mixture (Fig. 5) confirm the existence of the Cr(VI)–PSAA complex (I) having direct S–Cr bond.\(^{61}\)

On the basis of the above observed experimental results, the nucleophilic attack of sulfur atom of PSAA on the chromium atom of the oxidizing species, HCrO_3^- is proposed as the initial step of the mechanism (Scheme 1). As a result of nucleophilic attack of PSAA, a positive charge is developed on the sulfur center in the transition state (I).

The observed substituent effects and negative values of \( \rho \) afford positive evidence for the formation of PSAA–Cr(VI) intermediate, (I) and also support its formation as a slow rate determining step. From the above mechanism it
is clear that electron releasing substituents in PSAA stabilize the sulfonium ion intermediate, (I) formed in the rate determining step through resonance interaction besides facilitating the nucleophilic attack of PSAA on chromium atom (Eqn. 5). Thus electron releasing groups attached to the phenyl group of PSAA facilitate the formation of intermediate (I) by enhancing the nucleophilic ability of PSAA and thereby the reaction rate. On the contrary, the reverse effects are operating in eqn. (5) by electron withdrawing substituents. Thus one could expect a change in rate from acceleration to retardation, upon changing the substituents from electron releasing to electron withdrawing.

Such type of S$_{N}$2 nucleophilic attack is evidenced from the insignificant change in reaction rate in the presence of varying concentration of radical scavenger, acrylamide from $0.5 \times 10^{-2}$ mol dm$^{-3}$ to $5.0 \times 10^{-2}$ mol dm$^{-3}$ which also eliminates the possibility of single electron transfer mechanism leading to the formation of organic free radicals. The $\rho$ values observed by altering the electronic nature of substituents in PSAA in this reaction (Table 2) also well agree with the $\rho$ values observed in other S$_{N}$2 type reactions involving organic sulfur compounds$^{64-66}$ thus favouring the proposed mechanism. Generally, single electron transfer processes are characterized by low $\rho$ values.$^{67,68}$ Further, the successful application of reactivity-selectivity principle, which cannot be applied for one electron transfer reactions, strongly supports the S$_{N}$2 type nucleophilic attack leading to the formation of PSAA–Cr(VI) complex. The existence of PSAA–Cr(VI) complex in the rate determining step but not complete transfer of two electrons from PSAA to Cr(VI) leading to the formation of Cr(IV) in a slow step is also inferred from the absence of any significant change in reaction rate with the addition of Mn$^{2+}$ ($1.0 \times 10^{-3}$ to $50 \times 10^{-3}$ mol dm$^{-3}$) to the reaction mixture.

The association of reactant molecules in the rate determining step to form a considerably rigid transition state (intermediate I) with the decrease in degrees of freedom of the molecules is also suggested on the basis of the observed negative entropy of activation values (Table 2). Another observation noted is that, p-Cl PSAA has the lowest negative entropy of activation ($-18.57$ JK$^{-1}$ mol$^{-1}$) in the present series of reactants while p-OCH$_3$ PSAA has the highest value ($-54.31$ JK$^{-1}$ mol$^{-1}$). It is also noted that the calculated entropy of activation for the reaction of PSAA at 20% CH$_3$CN – 80% H$_2$O mixture is $-19.28$ JK$^{-1}$ mol$^{-1}$ and that at 40% CH$_3$CN – 60% H$_2$O is $-24.49$ JK$^{-1}$ mol$^{-1}$.

The development of positive charge on the sulfur atom of PSAA in the PSAA – Cr(VI) complex (I) facilitates the formation of intermediate (II) by ligand coupling between O and S$^{15,19,42}$ with the simultaneous C$\alpha$–C$\beta$ bond cleavage$^{69}$ leading to the elimination of CO$_2$ in a fast step. The liberation of CO$_2$ during the course of the reaction is confirmed using the method reported by Crossno et al.$^70$ The presence of phenyl group attached to the positively charged sulfur center in (I) further accelerates the formation of intermediate (II). Subsequently, the intermediate (II) undergoes a redox decomposition with a two electron transfer in a fast step that leads to the formation of products, methyl phenyl sulfone and Cr(IV) (Scheme 1).

Scheme 1. Oxidative decarboxylation of PSAA by Cr(VI).

The excellent plots of Hammett correlation obtained between second order rate constants and $\sigma$ values along with the isokinetic relationship and successful operation of reactivity-selectivity principle unam-
biguously prove that all the substituted PSAAs follow the same mechanism in the present reaction series.

The Cr(IV) species formed in this step undergoes disproportionation in the subsequent fast steps leading to the final product Cr(II). Such a sequence of reactions in Cr(VI) oxidations is well known and different ways of disproportionation have been proposed by different researchers. Westheimer proposed the following type of disproportionation reaction:

\[
\text{Cr(IV)} + \text{Cr(VI)} \to 2\text{Cr(V)} \tag{7}
\]

\[
\text{Cr(V)} + \text{PSAA} \to \text{MeSO}_2\text{Ph} + \text{Cr(III)} \tag{8}
\]

Though the oxidation of Cr(IV) by Cr(VI) is thermodynamically unfavourable, the transient Cr(IV)-aqua species reacts with Cr(VI) very fast. In strongly acidic media, the process of structure-reactivity principle confirm that all the meta- and para-substituted phenylsulfinylacetic acids follow Westheimer’s mechanism (Eqs. 7 and 8).

CONCLUSION

The active oxidizing species of Cr(VI) in the oxidative decarboxylation of PSAA is found to be HCrO$_3$. The proposed mechanism involving rate determining nucleophilic attack of sulfur on chromium followed by fast ligand coupling and decarboxylation are in conformity with the product analysis and kinetic studies. An excellent Hammett correlation is obtained for the meta- and para-substituted phenylsulfinylacetic acids. The existence of isokinetic relationship and the operation of structure-reactivity principle confirm that all the meta- and para-substituted phenylsulfinylacetic acids follow the same mechanism.

Acknowledgments. The publication cost of this paper was supported by the Korean Chemical Society.

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### Appendix II

Table of substituent parameters employed in Hammett correlation

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Substituent</th>
<th>$\sigma_p$ [1]</th>
<th>$\sigma_m$ [1]</th>
<th>$\sigma_p^{+/−}$</th>
<th>$\sigma_m^+$</th>
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<td>H</td>
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<td>-0.02 [2]</td>
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<tr>
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<td>0.40 [2]</td>
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<tr>
<td>8.</td>
<td>Br</td>
<td>0.23</td>
<td>0.39</td>
<td>0.17 [2]</td>
<td>0.35 [2]</td>
</tr>
</tbody>
</table>
Statistical methods in correlation analysis and evaluation of errors in kinetic data

All measurements are inevitably accompanied by errors. For the numerical findings of any study to furnish valid and meaningful results, the precision and significance of the data have to be evaluated by means of statistical tests [6]. Hence all the data obtained in the kinetic study of the present investigation were analyzed by regression analysis and a brief account of the statistical procedure employed is presented below.

Simple regression

If a series of values of a dependent variable Y are suspected to be linearly related to the independent variable X, Y is plotted against X [7]. The equation of the straight line may be written as

\[ Y = a X + b \]  

where ‘a’ is the slope of the line and ‘b’ is the intercept on the Y axis. The values of ‘a’ and ‘b’ can be obtained by the method of least-squares as follows. For ‘n’ pairs of values of Y and X (data sets), the following equations are defined for convenience in calculation [8].

\[ \sum u^2 = \sum (X - \bar{X})^2 = \sum X^2 - n \bar{X}^2 = \sum X^2 - \frac{(\sum X)^2}{n} \]  

\[ \sum v^2 = \sum (Y - \bar{Y})^2 = \sum Y^2 - n \bar{Y}^2 = \sum Y^2 - \frac{(\sum Y)^2}{n} \]  

\[ \sum uv = \sum (X - \bar{X})(Y - \bar{Y}) = \sum XY - n \bar{X} \bar{Y} = \sum XY - \frac{\sum X \sum Y}{n} \]
Then, the slope ‘$a$’ and the intercept ‘$b$’ are given by eq.5 and eq.6.

$$a = \frac{\sum uv}{\sum u^2}$$  \hspace{1cm} (5)$$

$$b = \frac{1}{n} (\sum Y - a \sum X)$$  \hspace{1cm} (6)$$

The simplest measures of the success of the correlation are the standard deviation of the regression ‘$s_{Y.X}$’ and the correlation coefficient ‘$r$’. They are given by the following eq.7 and eq.8.

$$s_{Y.X} = \left(\frac{\sum v^2 - a^2 \sum u^2}{n-2}\right)^{1/2}$$  \hspace{1cm} (7)$$

$$r = \frac{\sum uv}{[\sum u^2 (\sum v^2)]^{1/2}}$$  \hspace{1cm} (8)$$

Then, the variance of the regression coefficient of the standard deviation of ‘$a$’ is given by eq. (9).

$$s_{a_{YX}}^2 = \frac{s_{YX}^2}{\sum u^2}$$  \hspace{1cm} (9)$$

$$s_{a_{YX}} = [s_{YX}^2 / \sum u^2]^{1/2}$$  \hspace{1cm} (10)$$

Confidence limits (CL) for ‘$a$’ are calculated in terms of student’s t-values by eq.11.

$$\text{CL for } a = a \pm t_a \frac{s_{a_{YX}}}{\sqrt{n}}$$  \hspace{1cm} (11)$$
where $\psi$ represents the number of degrees of freedom (n-2) and denotes the significance level of the student’s t-test. In the present study 95% CL is used in the calculations unless specified otherwise.

**Evaluation of errors in activation parameters**

In the present study, the $\Delta^\dagger H$ and $\Delta^\dagger S$ values were calculated from the slope and intercept of a least square fit of the Eyring’s eq.12.

\[
\log \frac{k}{T} = 10.319 + \frac{\Delta^\dagger S}{4.576} - \frac{\Delta^\dagger H}{4.576 T}
\]

(12)

Petersen et al. [9] have shown that the error in $\Delta^\dagger S$ ($\sigma$) is directly proportional to the error in $\Delta^\dagger H$ ($\delta$) which may lead to a fortuitous linear correlation between $\Delta^\dagger H$ and $\Delta^\dagger S$. Hence, the errors in $\Delta^\dagger H$ and $\Delta^\dagger S$ were calculated using eq.13 and eq.14 given by Petersen et al. [9].

The error in $\Delta^\dagger H$ is,

\[
\delta = \frac{2RT'T}{T' - T} \alpha
\]

(13)

where $\alpha$ is the maximum fractional error in the rate constants, R is the gas constant in Joules, T and T’ are the two extreme temperatures at which the reaction is studied.

The error in $\Delta^\dagger S = - \sigma = \delta \frac{1}{T} + \frac{T' - T}{2T'T}$

(14)

According to Petersen et al. [9] the $\Delta^\dagger H - \Delta^\dagger S$ relationship is valid only when the observed range of $\Delta^\dagger H$ is greater than 2 $\delta$. 


References


