Kinetics and mechanism of oxidative degradation of DL-serine by chromium(VI)

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The oxidation kinetics of DL-serine by Cr(VI) has been studied spectrophotometrically in aqueous sulphuric acid. The reaction occurs through the path:

slow

\[
\text{HO-CH}_{2}-\text{CH(NH)}_{2}-\text{COOH} \rightarrow \text{OHC-CH(NH)}_{2}-\text{COOH}
\]

fast

\[
\rightarrow (\text{NH})_{2}\text{CH}_{2}\text{-COOH}+\text{CO}_{2}
\]

An intermediate, 2-amino-3-oxo propanoic acid, has been identified as its hydrazone derivative. The net rate law, as measured by the formation of Cr(III), is given by:

\[
k_{\text{obs}} = k_{1}K_{\text{es}}[\text{H}_{2}\text{SO}_{4}][\text{DL-serine}]_{T}
\]

The values of \(k_{1}\) and \(K_{\text{es}}\) have been evaluated at different acidities. Mechanism with the associated reaction kinetics is assigned and discussed.

The kinetics and mechanism of electron transfer reactions (chromic acid oxidations) of sulphur and oxygen containing organic substrates have been investigated extensively\(^7\). The phenomenon of ligand replacement as a prerequisite to redox processes has been discussed\(^8\) as has the correlation between the rates of oxidations by o xoanions and those of their ligand-exchange reactions. Coordination of the reductant to the metal centre is a step preceding oxidation has been observed in several instances\(^9\). Most commonly, mechanistic deductions have been drawn from the observations of changes in kinetic data that occurred when the structure of the organic substrate was altered in some way\(^8\). It is thought that breakdown of biologically important amino acids using Cr(VI) as oxidant would be worth studying. This note deals with the kinetics of oxidation of DL-serine by Cr(VI) in acid medium.

Serine is a special amino acid which has primary \(-\text{OH}\) group in addition to the ammonium group on the carbon chain. In effect, carbon skeleton of serine is more oxidized than that of other amino acids (except sulphur containing). The main objective of the present investigations is to elucidate suitable mechanism and to put forward a rate law consistent with experimental data.

Experimental

DL-Serine (chromatographically homogeneous, BDH), potassium dichromate (Sigma), sulphuric acid (-98% Merck), potassium sulphate (Fluka), manganese sulphate (Fluka) and acrylonitrile (Sigma) were used without further purification. Solutions of all the reagents were prepared in doubly distilled water.

The method has been detailed elsewhere\(^1\). The progress of the reaction was followed by monitoring formation of one of the products, Cr(III), at 575 nm. Pseudo-first order conditions were maintained in all runs with excess DL-serine (\(\geq 10X\)). The pseudo-first order rate constants \(k_{\text{obs}}\) were determined from the linear part of plots of log \(\frac{(A_{0}-A_{t})}{(A_{0}-A_{\infty})}\) versus time where \(A_{0}=\text{absorbance at zero time, } A_{t}=\text{absorbance at time, } t.\) Such plots were linear for at least 80% completion of the reaction and duplicate measurements agreed to \(\pm 2\%\).

A solution of potassium dichromate (0.01 mol dm\(^{-3}\), 2 cm\(^3\)) in 0.5 mol dm\(^{-3}\) \(\text{H}_{2}\text{SO}_{4}\) was added to a mixture of the DL-serine (0.1 mol dm\(^{-3}\), 4 cm\(^3\)) and 23% (v/v) acrylonitrile (1.0 cm\(^3\)) at 50°C. After 40 min a white precipitate of polymer appeared slowly. Experiments conducted at high [\(\text{H}_{2}\text{SO}_{4}\)] (\(\geq 6.0\) mol dm\(^{-3}\)) as well as blank experiments (without added DL-serine) did not show formation of such a white precipitate. The inability to detect free radicals in high acidic solutions is in agreement with previously reported results\(^10\).

The main product, glycine, was characterized as follows: DL-serine (0.01 mol dm\(^{-3}\), 5 cm\(^3\)) in 0.5 mol dm\(^{-3}\) \(\text{H}_{2}\text{SO}_{4}\) was added to a solution of potassium dichromate (0.1 mol dm\(^{-3}\), 5 cm\(^3\)) at 30°C. The reaction mixture was stirred for 12 h. Sodium...
hydroxide was added until the pH of reaction mixture became 5.0, and glycine was then estimated with standard ninhydrin method. Formation of glycine was also confirmed by the chromotropic acid. Reduction of chromium(VI) was not observed after prolonged incubation in the presence of glycine and H₂SO₄ which indicated that oxidation of glycine by chromium(VI) is not possible under our experimental conditions. This is an additional support for the oxidation product of DL-serine.

The intermediate, 2-amino-3-oxo propanoic acid was detected by the following method: An ice cold solution of DL-serine (0.5 gm) in H₂SO₄ (18 mol dm⁻³, 6 cm³) and 5 cm³ saturated aqueous potassium dichromate were added to a 2,4-dinitrophenyl hydrazine acid solution (0.3%, 25 cm³). After 1h, the reaction mixture was filtered out and the yellow residue was washed with ethanol and recrystallized by acetic acid. The compound was analysed by IR spectra and was identified as the 2,4-dinitrophenylhydrazone of 2-amino-3-oxo propanoic acid. (vNH₂=3200-2800, vCOO (as)=1600 and vC=N=1650 cm⁻¹). The melting point of the hydrazone was found to be 170°C.

The formation of CO₂ was estimated qualitatively as described elsewhere.

Results and discussion

The stoichiometry of the reaction between K₂Cr₂O₇ and DL-serine in the presence of H₂SO₄ was determined using spectrophotometric titrations. The spectra of reaction mixture containing various concentrations of chromium(VI) and fixed [DL-serine] were measured after the completion of the reaction. The absorbance of remaining chromium(VI) was monitored at 475 nm (at this wavelength, chromium(III) has negligible absorbance). The stoichiometry was found to be 1:4 i.e. one mole of oxidant was consumed by 4 mol of reductant.

At different [Cr(VI)] i.e., 1.0, 1.5 and 2.0×10⁻³ mol dm⁻³ but fixed [DL-serine] (0.1 mol dm⁻³) the values of pseudo-first order rate constants were found to be constant with increase in [Cr(VI)] (Table 1) indicating that the total [Cr(VI)] must be used in the rate law with first order dependence on [Cr(VI)]. The rate law is, therefore, as in Eq. (1):

\[ d[Cr(III)]/dt = -d[Cr(VI)]/dt = k_{obs}[Cr(VI)] \]

The effect of varying [DL-serine] (0.02-0.20 mol dm⁻³) on the reaction rate was studied at a fixed [Cr(VI)] (1.0×10⁻³ mol dm⁻³) as a function of H₂SO₄. The results are presented in Table 1. It is observed that as [DL-serine] increases, \( k_{obs} \) increases but non-linearly (Fig. 1). A marked curvature is observed in all the cases indicating outer sphere complexation between the reactive species. DL-serine participates in acid-base equilibria:

\[
\begin{align*}
K_1 & : \text{HO-CH}_2-\text{CH(NH}_3^+\text{-COOH}=\text{HO-CH}_2-\text{CH(NH}_3\text{-COO}+H^+} \\
K_2 & : \text{HO-CH}_2-\text{CH(NH}_3\text{-COOH}=\text{HO-CH}_2-\text{CH(NH}_3\text{-COO}+H^+}
\end{align*}
\]
NOTES

**Fig. 3** — Absorption spectra of [Cr(VI)] in different [H$_2$SO$_4$]; [Cr(VI)]=0.0028 mol dm$^{-3}$; [H$_2$SO$_4$]=1, 0.035, 2, 2.0, 3.4, 4, 6.04, and 5, 8.05 mol dm$^{-3}$

From the $pK_a$ values (2.2 and 9.4) one can ascertain that, under the present experimental conditions of acidity, [H$_2$SO$_4$]=2.0 to 8.0 mol dm$^{-3}$, the monopositive species exists in significant concentration.

The reaction was studied as a function of [H$_2$SO$_4$] between 1.0x10$^{-6}$ and 8.0 mol dm$^{-3}$ at various fixed [DL-serine] and constant [Cr(VI)], (1.0x10$^{-3}$ mol dm$^{-3}$) at 30°C. No oxidation of DL-serine was observable at lower acidity (1.0x10$^{-6}$-1.0x10$^{-2}$ mol dm$^{-3}$), even after prolonged incubation at 30°C. Since we found no significant reaction at short reaction times at [H$_2$SO$_4$]=1.3x10$^{-2}$ mol dm$^{-3}$, the reaction was carried out in highly acidic medium (2.0≥[H$_2$SO$_4$]≤8.0). These results confirm that the reductant (DL-serine) reacts with Cr(VI) at a significant rate only when it is protonated or must supply Cr(VI) with a proton$^4$. These results are in close agreement with the observations on oxidation of lactate$^8$, oxalate and formate$^1$ by the same oxidant at low pH which also failed to reduce Cr(VI) at higher pH.

The plot of rate constant versus [H$_2$SO$_4$] was a curve passing though the origin (Fig. 2). Further, a log-log plot was linear with slope 2.0 indicating the order in to [H$_2$SO$_4$] to be two. The absorption spectra of mixtures containing the same Cr(VI) and H$_2$SO$_4$ in different molar ratios exhibited different absorptions at same $\lambda_{max}$=450 nm (Fig. 3). The absorbance decreases with increase in [H$_2$SO$_4$] indicating that major portion of the existing species, Cr$_2$O$_7^{2-}$, is converted into HOCrO$_2$OSO$_3$H.

To find out the presence of Cr(IV) involved in the rate-limiting step, reaction rates were measured in the presence of varying [Mn(II)] (Table 1). The rate constant remained unchanged. Mn(II) had no effect on the reaction rate, this would suggest that the oxidant in this reaction is not involved after the rate-determining steps. Disproportionation of chromium(IV) is assumed to take place. A similar observation was made by Haight and co-workers$^{10}$. However, a different role of Mn(II) can be seen as in extremely high-acid solutions no inhibition by Mn(II) would be expected$^{15}$.

On the basis of the above results, a mechanism, shown in Scheme 1, has been proposed for the oxidation of DL-serine with Cr(VI).

As soon as one molecule of DL-serine enters into the inner coordination sphere and OS is formed, the coordination of second molecule of DL-serine would make the central chromium atom more positive and thereby increase the tendency of the chromium to

<table>
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<th>$10^3$[Cr(VI)]$_T$</th>
<th>$10^{-3}$[H$_2$SO$_4$]</th>
<th>$10^{-3}$[Mn(II)]</th>
<th>$10^{-3}$[DL-serine]</th>
<th>$10^8 k_{obs}$</th>
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oxidize the coordinated DL-serine. This argument is very similar to the observations made by Natile et al.\textsuperscript{16} and confirms that the interaction of second DL-serine molecule with chromate-DL-serine ester (OS) is not a rate determining step.

The rate law corresponding to Scheme 1 can be expressed as Eq. (2)

\[ \text{Rate} = \frac{d [\text{Cr(III)}]}{dt} = k_{\text{obs}} [\text{OS}] [\text{H}_2\text{SO}_4] \]  

which on comparison with Eq. (1), gives Eq. (3).

\[ k_{\text{obs}} = \frac{k_1 K_{\text{es}} [\text{H}_2\text{SO}_4]^2 [\text{DL-serine}]_T}{1 + K_{\text{cal}} [\text{DL-serine}]_T} \]  

Accordingly plots of \( k_{\text{obs}} \) versus \([\text{H}_2\text{SO}_4]^2\) at constant [DL-serine]\(_T\) should be linear. This has been found to be so.

Equation (3) can be rewritten as (4)

\[ \frac{1}{k_{\text{obs}}} = \frac{1}{k_1 K_{\text{es}} [\text{H}_2\text{SO}_4]^2 [\text{DL-serine}]_T} + \frac{1}{k_1 [\text{H}_2\text{SO}_4]^2} \]  

The values of \( k_1 \) and \( K_{\text{es}} \) have been calculated from the intercepts and slopes of the plots of \( 1/k_{\text{obs}} \) versus \( 1/[\text{DL-serine}]_T \) at constant \([\text{H}_2\text{SO}_4]\) and are given in Table 2. The rate constants have been calculated \( (k_{\text{cal}}) \) in various kinetic runs by substituting the values of \( k_1 \) and \( K_{\text{es}} \) in Eq. (3) and compared with the \( k_{\text{obs}} \) values (Table 1). The close agreement between the \( k_{\text{obs}} \) and \( k_{\text{cal}} \) provides the supporting evidence for the proposed mechanism. Oxidation of DL-serine by Cr(VI) occurs in two kinetically distinguishable steps. The first is a rapid ester formation between DL-serine and Cr(VI) and the second, a slower electron transfer step. The Burk Lineweaver-type double reciprocal plots (i.e. \( 1/k_{\text{obs}} \) versus \( 1/[\text{DL-serine}]_T \)), indicate association of the oxidant and substrate in some pre-equilibrium steps before the electron-transfer step and also satisfy the Michaelis-Menton\textsuperscript{17} reciprocal relationship (kinetic proof for complex formation). Hence a complex formation between DL-serine and reactive species of Cr(VI) occurs \textit{a priori}.

The reaction was studied as a function of temperature between 30 to 45°C to evaluate the activation parameters (Table 2). Large negative values of \( \Delta G^\circ \) indicate existence of compact activated state stabilized by strong hydrogen bonding and large solvation in the electron transfer step. Although

### Table 2 — Values of rate constant \((k_1)\) ester formation constant \((K_{\text{es}})\), activation and thermodynamic parameters for the oxidation of DL-serine with Cr(VI)

<table>
<thead>
<tr>
<th>([\text{H}_2\text{SO}_4])</th>
<th>(10^4 k_1)</th>
<th>(K_{\text{es}})</th>
<th>(\Delta H^\circ)</th>
<th>(\Delta S^\circ)</th>
<th>(\Delta G^\circ)</th>
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<tbody>
<tr>
<td>mol dm(^{-3})</td>
<td>mol(^{-1}) dm(^{3}) s(^{-1})</td>
<td>mol(^{-1}) dm(^{3})</td>
<td>kj mol(^{-1})</td>
<td>JK(^{-1}) mol(^{-1})</td>
<td>kj mol(^{-1})</td>
</tr>
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<td>2.3</td>
<td>-318.3</td>
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<td>-2.1</td>
</tr>
</tbody>
</table>

\([\text{H}_2\text{SO}_4]\) | \(\Delta H^\circ\) | \(\Delta S^\circ\) | \(\Delta G^\circ\) |
| mol dm\(^{-3}\)  | kj mol\(^{-1}\) | JK\(^{-1}\) mol\(^{-1}\) | kj mol\(^{-1}\) |
negative entropy of activation is a characteristic of rate-limiting formation of an intermediate complex (i.e. ester), decomposition of the chormic ester (in the case of mandelic acid) was still postulated as the rate limiting\textsuperscript{18,19}. In the present case, the values of ester formation constant ($K_{eq}$) and rate constant ($k_1$) indicate that the decomposition of the chormic ester of DL-serine is also a rate-limiting step due to the observed Michaelis-Menton kinetics.

These results suggest that the DL-serine can be converted into glycine after the oxidation of $\text{-OH}$ group of DL-serine by chromium(VI). Glycine does not react with inorganic oxidants, Mn(II) and Cr(VI) (at least under the conditions of this work).

References


1 Carri
2 Ari