Kinetics of oxidation of ethylenediaminetetraacetic acid (EDTA) by chromium(VI) in the presence of perchloric acid

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The kinetics of the oxidation of EDTA by Cr(VI) in the presence of perchloric acid has been followed by visible spectrophotometry at 350 nm. The effects of the total [Cr(VI)], [EDTA] and [HClO4] on the rate are determined. The reaction is first-order each in [Cr(VI)] and [EDTA] whereas the rate-[H+] profile suggests complicated kinetic features. Addition of Mn(II) has a large accelerating influence. These observations permit to propose detailed mechanism for the oxidation of EDTA by Cr(VI) in the presence and absence of Mn(II). The catalytic effect of Mn(II) has been ascribed to a one-step, three-electron process in which a termolecular complex is formed between the oxidant, Mn(II) and EDTA. The oxidation has the rate expression:

\[ -d[Cr^{VII}] / dt = k_1 K_w [H^+]^2 K_1 [Cr^{VIII}]_1 [EDTA]_1 / \{ / [H^+] + K_3 + K_4 / [H^+] \} \]

Ethylenediaminetetraacetic acid (EDTA) is a multifunctional \( \alpha \)-amino acid that behaves as a double zwitterion in dilute aqueous solution and has a very low solubility in water. EDTA has a wide general application in analysis because of its powerful complexing action and commercial availability. It is used as chelating agent in the treatment of heavy metal poisoning, for example, when children ingest chipped paint that contains lead and also for the determination of calcium(II) in blood. Therefore, its susceptibility to biodegradation during waste-water treatment and in the aquatic environment is an important criterion for assessing its environmental impact and toxicity. Imidodiacetate was reported to be an intermediate in the biodegradation pathway of EDTA.

Decomposition of EDTA-manganese(III) complex was reported by Pribil et al. which was enhanced by light, heat and manganese(II). EDTA is capable of acting as quadridentate-, quinquedentate-, or sexidentate ligand. Its disodium salt reacts with metal ions. The reaction with cations, e.g., M\(^{3+}\), may be written as,

\[ M^{3+} + EDTA \rightarrow EDTA-M + 2H^+ \]

This equation indicates that there is always a competition in the solution between metal ions and hydrogen ions seeking the negative sites on EDTA. The hydrogen ion concentration (or pH) of the solution has, therefore, a marked influence on the stability of a metal-EDTA complex.

The kinetics of acid dichromate oxidation of several organic substrates are well-documented in the literature but the use of complexing agents in a similar study is rare. Mitewa et al. have earlier pointed out in their pioneering review that the mechanism of the catalytic action of EDTA, picolinic acid, 2,2'-bipyridyl, 1,10-phenanthroline and other polynuclear acids is unclear. Beck et al. have reported the role of EDTA in the chromium(VI) oxidation of hydrazine but no attempt was made to determine the kinetic relationships. For lack of information on similar studies using EDTA as an oxidant, we report herein the results of the title investigation using EDTA as the substrate in acid medium both in the absence and in the presence of manganese(II).

Materials

Reagent grade ethylenediaminetetraacetic acid disodium salt (98%, s.d. fine, India), potassium dichromate (99%, Merck, India) and manganese(II) chloride (99%, Qualigens, India) were used to prepare their stock solutions. The solution of EDTA was stored in polyethylene bottle as its solution gradually leaches metal ions from glass containers, resulting in a change in the effective concentration of EDTA. To maintain the [H\(^+\)] constant, perchloric acid (Fisher, 70% reagent) was used. The solution of potassium dichromate was stored in a dark glass bottle. Double distilled (first time from alkaline KMnO\(_4\), CO\(_2\)-free,
deionised water was used for dilution and for the preparation of stock solutions of all the reactants.

Kinetic measurements. The reactions were started in glass-stoppered two-necked flask fitted with a spiral double-walled condenser to check evaporation. A mixture containing required amounts of EDTA, HClO₄ and H₂O was thermally equilibrated at 25.0±0.1 °C and to this was added a measured amount of chromium(VI) solution, pre-equilibrated at the same temperature. The reaction volume was always 50 cm³. The course of the reaction was monitored by measuring the absorbance of the remaining chromium(VI) at definite time intervals at 350 nm against blanks containing all the constituents except chromium(VI) on a Spectronic 21-D Spectrophotometer. The reaction was normally followed up to 80% completion. The pseudo-first order rate constants (kₜₐₚ, s⁻¹) were computed from the slopes of the plots of log(absorbance) versus time. The values of r (linear regression coefficient) were ≥ 0.995 for all the kₜₐₚ. Other experimental details were the same as described elsewhere²⁵,²¹.

Product analysis. For characterization of chromium(VI) reduction product, EDTA (=2.0 × 10⁻² mol dm⁻³), HClO₄ (=1.16 mol dm⁻³), and chromium(VI)- (=5.0 × 10⁻³ mol dm⁻³) were mixed at room temperature (=25°C). Although visual observation indicated that the reaction was over in 20 – 40 min, the mixture was kept for ca. 60 min and then the UV-vis spectra were recorded (Figure 1). The yellow-coloured reaction mixture (Figure 1a) became purple in the presence of EDTA at the end of the reaction (Figure 1b). The most characteristic part of chromium(III) spectrum is the two d-d transitions observable in the 350-600 nm region. Our spectra consists of two broad bands with λ_max = 400 and 550 nm. These results indicate that EDTA coordinates with chromium(III) species. Our λ_max values are in good agreement with the literature values²¹. The quinquedentate nature of the chromium(III) -EDTA complex [Cr(III) YH (H₂O), EDTA = Y⁻], was confirmed by IR spectroscopy which showed that a non-complexed –COOH group was present. It may be assumed that the potentially pentadentate ethylenediaminetetra-acid should yield a very stable chromium(III) complex with a very similar visible spectrum to that of the EDTA complex. Direct observation of mixtures of chromium(III) nitrate and EDTA showed that the reaction was slow at the usual hydrogen ion concentrations of such mixtures²². Thus, it is confirmed that EDTA must coordinate with chromate ion and be present in the inner coordination sphere of chromium ion with valency higher than three.

Carbon dioxide and formaldehyde were identified by the reported methods as the other reaction products.
Results and Discussion

Stoichiometry measurements. The composition of the purple coloured complex was determined by Job’s method of continuous variations. For this purpose, solutions of chromium(VI) and EDTA were mixed, kept in a thermostat at 25 °C for 90 min and then their absorbance were recorded at 550 nm. The composition was found to be 4:5, i.e., ca. one mole of chromium(VI) react with 1.25 moles of EDTA to give chromium(III)-EDTA complex as the final product. Due to the complex kinetic behaviour exact stochiometric equation can not be predicted.

Reaction-time curve. The log (absorbance) versus time plots indicate clearly that the redox process has induction period (no reaction) followed by autoacceleration. \(^{2,5}\) (Figure 2). It was observed that the extent of the induction period depended on the reaction conditions, i.e., \([\text{HClO}_4]\) (Figure 2, Set A) and [EDTA] (Figure 2, Set B). It was observed that the plots of log (absorbance) versus time had the general shape shown in Figure 2 which indicates apparent complexity of the EDTA oxidation by chromium(VI). The absorbance of the chromium(VI) remains constant for some time, after which there is sharp decrease. The time for commencement of the change in absorbance depends upon the reaction conditions (Table I), i.e., \([\text{HClO}_4]\) and [EDTA].

Rate dependence on \([\text{HClO}_4]\). The effect of \([\text{H}^+]\) on the rate of EDTA decomposition (second step, autoacceleration) was studied as a function of \([\text{HClO}_4]\) between 0.11 and 2.32 mol dm\(^{-3}\) at constant [EDTA] (2.0 × 10\(^{-2}\) mol dm\(^{-3}\)), [Cr(VI)] (1.0 × 10\(^{-4}\) mol dm\(^{-3}\)) and temperature (25 °C). The rate increased with the increase in \([\text{HClO}_4]\) (Table I).

Rate dependence on [EDTA]. The order with respect to [EDTA] was deduced from the experiments performed at several [EDTA] with fixed chromium(VI) and HClO\(_4\) concentrations. The [EDTA] was varied in the range (1.0 - 6.0) × 10\(^{-2}\) mol dm\(^{-3}\) ([Cr(VI)] = 1.0 × 10\(^{-4}\) mol dm\(^{-3}\), \([\text{HClO}_4]\) = 1.16 mol dm\(^{-3}\), 25 °C). The results (Table I) indicate that the order with respect to EDTA is one.
Table I — Effect of [HClO₄], [Cr(VI)], and [EDTA] on the kₖₒᵦ for the oxidation of EDTA by chromium(VI) at 25°C.

<table>
<thead>
<tr>
<th>[HClO₄] mol dm⁻³</th>
<th>10²[Cr⁶⁺] mol dm⁻³</th>
<th>10⁴[EDTA] mol dm⁻³</th>
<th>Time of Induction period* (min)</th>
<th>10⁶ kₒᵦ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>1.0</td>
<td>2.0</td>
<td>No change in absorbance</td>
<td>0.0</td>
</tr>
<tr>
<td>0.11</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
<td>90</td>
</tr>
<tr>
<td>0.23</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
<td>70</td>
</tr>
<tr>
<td>0.69</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>1.16</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>1.39</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
<td>25</td>
</tr>
<tr>
<td>1.62</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>1.86</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>2.32</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>1.16</td>
<td>1.0</td>
<td>2.0</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>2.0</td>
<td>1.16</td>
<td>5.0</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>3.0</td>
<td>1.16</td>
<td>5.0</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>4.0</td>
<td>1.16</td>
<td>5.0</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>5.0</td>
<td>1.16</td>
<td>5.0</td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>6.0</td>
<td>1.16</td>
<td>5.0</td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

*No change in absorbance was observed during this period.

**Rate dependence on [chromium(VI)].** The invariance of rate constants over a variation in the initial [Cr(VI)]ᵦ (1.0 × 10⁻³ to 7.0 × 10⁻³ mol dm⁻³) at fixed [EDTA] = 2.0 × 10⁻² mol dm⁻³, [HClO₄] = 1.16 mol dm⁻³ and temperature = 25°C is indicative of first-order dependence of the reaction in [Cr(VI)]ᵦ (Table I). Thus, the reaction follows second order kinetics (first-order each in oxidant and EDTA). These results enable us to write the rate equation at constant acidity as:

\[ -d[Cr^{VI}]_T/dt = k_{obs} [Cr^{VI}]_T [EDTA]_T \]

where 'T' denotes total concentration.

**Mechanism**

It has been established that chromate oxidations generally fall into two categories:\[2]\:

(i) Initial reduction of chromium(VI) to chromium(IV) by two equivalent substrates.

(ii) Initial reduction of chromium(VI) to chromium(III) by three-equivalent substrates.

Accordingly, the following Scheme I can be proposed.

Before attempting to propose a mechanism, it is necessary to discuss on the species of EDTA existing in the HClO₄ medium. It has been reported\[26\] that EDTA behaves six coordinated in aqueous solutions and participates in the following acid-base equilibria:

\[
\begin{align*}
H_6Y^2+ & \rightleftharpoons K_{a1} H_5Y^+ + H^+ \\
H_5Y^+ & \rightleftharpoons K_{a2} H_4Y^- + H^+ \\
H_4Y^- & \rightleftharpoons K_{a3} H_3Y^- + H^+ \\
H_3Y^- & \rightleftharpoons K_{a4} H_2Y^2- + H^+ \\
H_2Y^2- & \rightleftharpoons K_{a5} HY^3+ + H^+ \\
HY^3+ & \rightleftharpoons K_{a6} Y^4- + H^+
\end{align*}
\]

where,

\[K_{a1} = 1.02 \times 10^{-2}; K_{a2} = 2.14 \times 10^{-3}; K_{a3} = 6.92 \times 10^{-7}\]

and \[K_{a6} = 5.50 \times 10^{-11}\].

The first two species (H₆Y²⁺ and H₅Y⁺) are relatively strong acids and normally are not of importance in evaluation of dissociation constants. Therefore, EDTA has only four values of dissociation constants. Under the experimental conditions used in this work ([HClO₄] = 0.11 - 2.32 mol dm⁻³), H₄Y species exists in significant concentration and this species is reactive.
Scheme II

towards complexation. The fractions of various forms (α) of EDTA in solution were calculated by using the relation

$$\alpha_1 = \frac{[H^+]}{B}; \alpha_2 = \frac{K_{a3}[H^+]}{B};$$

\(\alpha_3 = \frac{K_{a4}[H^+]^2}{B}; \alpha_4 = \frac{K_{a4}K_{a5}[H^+]^3}{B};\)

\(\alpha_5 = \frac{K_{a4}K_{a5}K_{a6}[H^+]^4}{B};\)

where \(B = [H^+]^4 + K_{a4}[H^+]^3 + K_{a4}K_{a5}[H^+]^2 + K_{a4}K_{a5}K_{a6}[H^+] + K_{a4}K_{a5}K_{a6}K_{a7}.\)
At pH 1.0, the values of \( \alpha_1, \alpha_2, \alpha_3, \alpha_4 \) and \( \alpha_5 \) were found to be 0.90, 0.092, 1.86 \times 10^{-3}, 1.3 \times 10^{-8} \) and 7.54 \times 10^{-18} respectively. On the other hand, chromic acid also participates in the acid-base equilibria\(^2\) and the only species possibly controlling the rate of oxidation seems to be \( \text{H}_2\text{CrO}_4 \). Hence, the steps of the oxidation can be written as shown in Scheme II.

In Scheme II, the \( \text{H}_2\text{Y} \) reacts with chromic acid to form an anhydride species (C1) through its \(-\text{COOH}\) groups\(^3\). The above mechanism is in close agreement with the results of various authors\(^5,8\) on decomposition of EDTA by manganese(II). Except the rate acceleration effect in the presence of \( \text{HClO}_4 \), we were unable to obtain any spectrophotometric evidence for a chromium(VI) complex with EDTA. The rate limiting step is a one-step, three-electron oxidation-reduction taking place in C1. The presence of electron-withdrawing group will increase the tendency of the chromium species C1 to accept electrons from the reducing agent EDTA. Therefore, the escaping tendency of \(-\text{COOH}\) group ultimately increased. On the basis of this mechanism the following kinetic Eq. 6 can be derived.

\[
\frac{d[\text{Cr}^{VI}]}{dt} = k_1[H^+]K_aK_i[\text{EDTA}](1/K_a) = k'_1[\text{EDTA}](1/K_a)
\]

and, for the first-order rate constants:

\[
k_{\text{obs}} = k_1/ K_a K_i[\text{EDTA}] = k'_1/K_a
\]

Equation (7) is in agreement with the experimental results for the reaction, since kinetic order in [EDTA] is unity.

**Effect of added manganese (II).** In order to confirm and get more insight into the reaction mechanisms shown in Schemes I and II, the effect of added manganese(II) was also studied because manganese(II) plays an important role in chromic acid oxidations and is used as a tool to determine the involvement of chromium(IV) as an intermediate\(^5,30,31\). The effect of [Mn(II)] on the reaction rate was studied in the presence of \( \text{HClO}_4 \) (1.15 mol dm\(^{-3}\)) over a fixed [EDTA] (2.0 \times 10^{-2} \text{ mol dm}^{-3}\) and [Cr(VI)] (1.0 \times 10^{-2} \text{ mol dm}^{-3}\) at 25 °C. As can be seen (Table II), the reaction is sensitive even to small concentrations of Mn(II). The effect that addition of Mn(II) to the solution resulted in a notable increase of the reaction rate is contrary to the general effect of Mn(II) on chromate oxidations where an inhibition is caused due to capture of chromium(IV) intermediate\(^5,30,31\). The positive catalytic effect is in conformity with the reduction \( \text{Cr(VI)} \rightarrow \text{Cr(III)} \) (one-step, three electron oxidation) without passing through formation of chromium(IV) as an intermediate. Therefore, the reaction mainly occurs through path II of Scheme I.

In the presence of manganese(II), the Scheme II mechanism can be modified as Scheme III.

The catalytic role of manganese(II) suggests its involvement in the rate-determining step. Thus, it forms an anhydride C4. The direct oxidation of manganese(II) ion by chromium(VI) is thermodynamically unfavourable\(^5\). The decomposition of EDTA-manganese(II)-chromate complex (C4) is due to the intramolecular electron transfer from the chelated EDTA to chromium(VI) and manganese(II), respectively. Time required for the internal redox reaction also decreased in the presence of manganese(II) (Table II).

Rate Equation (1) has been derived on the basis of Scheme III mechanism which shows a first-order dependence of the reaction on [Mn(II)] and [H\(^+\)], respectively.

\[
k_{\text{obs}} = k'/ K_{an} [\text{H}^+] [\text{C3}]
\]

**Conclusion**

The most interesting feature of this study is the oxidation of EDTA by chromium(VI). We are unaware of a precedence in the redox chemistry of EDTA. The constancy in the plots of log (absorbance) vs time in the EDTA oxidation is unique in the sense that the induction period has no reaction rate. Again, the reducing nature of EDTA may be explained by the outersphere complexation between EDTA and chromium(VI) (Scheme II); this type of behaviour is rare in the redox reactions involving intramolecular electron transfer from the chelated reductant to the oxidant. It is well established that complex formation results in considerable increase in the oxidation.

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**Table II — Effect of [Mn(II)] on the oxidation of EDTA (2.0 \times 10^{-2} \text{ mol dm}^{-3}\) by chromium(VI) (1.0 \times 10^{-3} \text{ mol dm}^{-3}\) at 25 °C and [HClO\(_4\)] = 1.15 mol dm\(^{-3}\).**

<table>
<thead>
<tr>
<th>[Mn(II)]</th>
<th>Time of induction period (min)</th>
<th>(10^4 k_{\text{obs}}) (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>30</td>
<td>3.8</td>
</tr>
<tr>
<td>0.4</td>
<td>22</td>
<td>8.2</td>
</tr>
<tr>
<td>1.0</td>
<td>18</td>
<td>18.5</td>
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<tr>
<td>1.5</td>
<td>16</td>
<td>40.2</td>
</tr>
<tr>
<td>2.0</td>
<td>15</td>
<td>68.2</td>
</tr>
<tr>
<td>3.4</td>
<td>8</td>
<td>Very fast</td>
</tr>
<tr>
<td>4.0</td>
<td>6</td>
<td>Very fast</td>
</tr>
</tbody>
</table>


potential of a metal ion\textsuperscript{32}. This is good reason to believe that the influence of \textit{–COOH} groups in the oxidation potential of chromium(VI) may have a profound effect on the oxidizing tendency of chromium(VI) in aqueous solutions. Secondly, the positive charge on complexes C\textsubscript{1} and C\textsubscript{4} may help to destabilize the higher valence state of chromium, \textit{i.e.}, six.

References
28 Shen-yang T & Li Ke-an, Talanta, 33, 1986, 775.