Kinetics and mechanism of oxidation of nitrilotriacetate by poly(pyridyl)iron(III) complexes and dodecatungstocobaltate(III) ion - A comparative study

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Kinetics of oxidation of nitrilotriacetate by Fe(IIW (L-phenanthroline or bipyridine) and CoW120~O have been investigated in aqueous acidic media. The reaction is first order each in reductant and oxidants but inversely proportional to acid concentration. The reactions are analysed by means of Schuster treatment of outer-sphere electron-transfer.

Amine N-polycarboxylates are used as chelating agents for the treatment of metal-overload conditions1. Thus the kinetics of iron removal from monoferric and cobalt-labelled monoferric human serum transferrin by nitrilotriacetate was reported2 recently. By contrast to its simple complexation stoichiometry, oxidation of nitrilotriacetate and its anions are complicated3 in terms of product distribution and stoichiometry.

We now report the stoichiometry, kinetics and mechanism of its oxidation by the encapsulated cobalt (III) complex, CoW12O405− and poly(pyridyl)iron (III) complexes, Fe(phen)3+ and Fe(bipy)3+ bearing in mind the points raised above.

Experimental
K5CoW12O40 and Fe(phen)3(CIO4)3, were prepared and characterised by literature methods4,5. Nitrilotriacetic acid (Aldrich) was used as received and its solutions were prepared fresh prior to kinetic and stoichiometric studies.

Kinetic studies
Kinetic studies were carried out by monitoring the rate of loss of the oxidant on a Unicam SP 1750 spectrophotometer fitted with thermostated cell compartments. The rates were measured at 390 nm (ref. 5) for CoW12O405−, 600 nm (ref. 4) for Fe(phen)3+ and 620 nm (ref. 4) for Fe(bipy)3+.

Rate constant for each exponential profile was evaluated from semilogarithmic plots of absorbance difference versus reaction time. Specific rates for replicate runs diverged by less than 3%.

Stoichiometric studies were carried out using procedures similar to those described elsewhere5.

Results and discussion

Stoichiometry and reaction products
Spectrophotometric examination of products in solution showed that the stoichiometries of the reactions are consistent with Eq. (1) where MIII are the trivalent oxidants, MII are their divalent analogues and H3nta is nitrilotriacetate

\[ 2M^{III} + H_3nta \rightarrow 2M^{II} + CO_2 + Other\ products \]  

The other products were found to be formaldehyde by phenylhydradine method6 and glycine by paper electrophoresis. From the mechanistic point of view, the product analysis suggests a reaction pathway in which C - N rather than C - C bond cleavage occurs. (MII were identified by their UV-vis spectral characteristics4,7).

Test for free radicals
Formation of free radicals during the reactions was confirmed by the appearance of a gel on adding a deaerated solution of acrylamide (5% w/v) to a deaerated reaction mixture followed by addition of a large excess of methanol. Since polymerization of acrylamide did not occur when it was added to the oxidants and the reductant solution separately, free radicals are formed during the reactions.

Kinetics and mechanism
Kinetic data for the oxidations appear in Table 1. With the reductant in excess in each case, rates are seen to be directly proportional to [reductant], indicating that the reactions are first order each in reductant. The reactions are also strongly inhibited by [H+], with the overall rate conforming to Eq (2).

\[ -d[M^{III}] /dt = 2 k[M^{III}] [H_3nta] / [H^+] \]  

Observed rate constants increased as a function of ionic strength in the reaction of Co^{III}W_{12}O_{40}^{5−}
Table 1—Kinetic data for the reactions of H$_3$nta with Co$^{III}$W$_2$O$_4$$^+$, Fe(phen)$_3$$^+$ and Fe(bipy)$_3$$^+$ at 25°C

<table>
<thead>
<tr>
<th>$[H_3n]_0$ (mol dm$^{-3}$)</th>
<th>$10^3$ $k_{obs}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$^{a}$Co$^{III}$W$_2$O$_4$$^+$</td>
</tr>
<tr>
<td>2</td>
<td>0.89</td>
</tr>
<tr>
<td>4</td>
<td>1.78</td>
</tr>
<tr>
<td>6</td>
<td>2.69</td>
</tr>
<tr>
<td>8</td>
<td>3.56</td>
</tr>
<tr>
<td>10</td>
<td>4.50</td>
</tr>
<tr>
<td>12</td>
<td>5.22</td>
</tr>
<tr>
<td>14</td>
<td>6.22</td>
</tr>
<tr>
<td>16</td>
<td>7.11</td>
</tr>
</tbody>
</table>

$^{a}$[H$^+$] = 1.0 mol dm$^{-3}$; $^{b}$[H$^+$] = 0.45 mol dm$^{-3}$; $^{c}$[H$_3$nta] = 0.01 mol dm$^{-3}$

With H$_3$nta but decreased for the reactions with Fe(phen)$_3$$^+$ and Fe(bipy)$_3$$^+$ (Table 2), suggesting positive and negative Bronsted-Debye effects respectively. Since the acid-dissociation constants of H$_3$nta are $K_1 = 2.00 \times 10^{-2}$; $K_2 = 3.798 \times 10^{-3}$ and $K_3 = 2.14 \times 10^{-10}$ mol dm$^{-3}$ the monoanion H$_2$nta is likely to be the predominant form of the reductant over the acid range investigated.

Thus the general mechanism which accounts for the empirical data may be postulated as

\[ \text{H}_3\text{nta} \rightarrow \text{H}_2\text{nta}^- + \text{H}^+ \quad \ldots (3) \]
\[ \text{M}^{III} + \text{H}_2\text{nta}^- \rightarrow \text{H}_2\text{nta}^- + \text{M}^{II} \quad \ldots (4) \]
\[ \text{M}^{III} + \text{H}_3\text{nta} \rightarrow \text{M}^{III} + \text{Other products} \quad \ldots (5) \]

where other products are CO$_2$, formaldehyde and glycine. This mechanism leads to the rate law given in Eq. (6) by applying the steady state approximation for [H$_2$nta].

\[ -d[\text{M}^{III}]/dt = 2K_1/([\text{H}^+ + K_1])k_2k_3[\text{M}^{III}]^2 \times [\text{H}_3\text{nta}]/k_2[\text{M}^{II}] + k_3[\text{M}^{III}] \quad \ldots (6) \]

Table 2—Dependence of reaction rate on ionic strength of the medium

<table>
<thead>
<tr>
<th>$I$ (mol dm$^{-3}$)</th>
<th>$10^3$ $k_{obs}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60</td>
<td>0.60</td>
</tr>
<tr>
<td>0.70</td>
<td>0.89</td>
</tr>
<tr>
<td>0.80</td>
<td>1.20</td>
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<tr>
<td>0.90</td>
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<td>1.00</td>
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</tr>
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<td>1.20</td>
<td>2.06</td>
</tr>
<tr>
<td>1.60</td>
<td>1.38</td>
</tr>
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<td>1.80</td>
<td>1.15</td>
</tr>
<tr>
<td>2.00</td>
<td>0.96</td>
</tr>
<tr>
<td>2.40</td>
<td>0.68</td>
</tr>
</tbody>
</table>

$^{a}[H^+] = 0.1$ mol dm$^{-3}$; $^{b}[H^+] = 0.45$ mol dm$^{-3}$; $^{c}[H^+] = 0.2$ mol dm$^{-3}$

where $[H_3nta] = [H_3nta]_0 (1 + K_1/[H^+])$

Since $[H^+] >> K_1$, if $1 >> K_1/[H^+]$ and $k_2[\text{M}^{III}] << k_3[\text{M}^{III}]$, the rate law simplifies to Eq. (7)

\[ -d[\text{M}^{III}]/dt = 2K_1k_2[\text{M}^{III}][\text{H}_3\text{nta}]_0/[H^+] \quad \ldots (7) \]

so that

\[ k_{obs} = 2K_1k_2[\text{H}_3\text{nta}]_0/[H^+] \quad \ldots (8) \]

Equations (7) and (8) are in agreement with the experimental rate law (2) where $k = K_1k_2$.

Using the value of $K_1 = 2 \times 10^{-2}$ (ref. 7), values of $k_2$, computed at different temperatures for each reaction together with the associated activation parameters are presented in Table 3.

In view of the facts that the reductant is used to remove overload of iron and cobalt$^2$ and the oxidants are substitution inert$^4,5,9$, one of the most interesting facets of this study is to ascertain
whether the reactions occur by the inner or outer-sphere mechanism. First, we tried Michaelis-Menten\textsuperscript{10} plots of $1/k_{\text{obs}}$ versus $1/[$reductant$]$. The intercept (if at all) in each case was within experimental uncertainty of zero, suggesting absence of kinetic evidence for appreciable amounts of reaction intermediates with inner-sphere character. Secondly, typical spectral scanning of the reactions showed isosbestic points, at 512 nm for $\text{C}_{\text{III}}\text{W}_{12}\text{O}_{40}^5^-$, 530 nm for $\text{Fe(phen)}_3^{3^+}$ and 530 nm for $\text{Fe(bipy)}_3^{3^+}$, indicating absence of oxidant-reductant intermediates.

It seems reasonable to surmise from the substitution inertness of the oxidants, the bulkiness of the substrate and absence of kinetic and spectroscopic evidence for inner-sphere type intermediates that the balance of evidence markedly favours the outer-sphere mechanism. Our results therefore collaborate those of Gibson and Vaughan\textsuperscript{11} who showed that nitrilotriacetate is the least effective ligand for binding Fe$^{\text{III}}$.

References