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Electron transfer reaction in the chromium(VI)-manganese(II) system in the presence of ethylenediaminetetraacetic acid (EDTA)

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Abstract

Upon addition of Cr^{VI} to a solution of ethylenediaminetetraacetic acid (EDTA) and Mn^{II}, a transient species appears which has an absorption maximum at 500 nm. Kinetic studies of the outer-sphere oxidation of the Mn^{II}-EDTA complex with the Cr^{VI}-EDTA complex have been investigated by visible spectrophotometry at 25 °C. The formation of a transient species has been characterized spectrophotometrically and the encounter complex formation constants have been determined ($K_{OS} = 1.75 \times 10^2$ and 1.66×10^3 mol^{-2} dm^6 for [EDTA] and [Mn^{II}] variations, respectively). The effect of total [EDTA], [Mn^{II}], [Cr^{VI}] and [$HClO_4$] on the rate of the reaction was determined. On addition of $HClO_4$, there is a decrease in the rate constants. The reaction product is the Cr^{III}-EDTA complex with $\lambda_{max} = 400$ and 550 nm. On the basis of the various observations and product characterization a most plausible *outer-sphere* mechanism has been envisaged.

Introduction

The reduction of chromium(VI) by various metal ions [iron(II), vanadium(IV), vanadium(III), neptunium(V), iridium(III) and molybdenum(IV)] has been the subject of investigations by a large number of researchers [1–10]. In the redox reactions of chromium with organic reductants, manganese(II) also plays an important role [11–15]. The formation of chromium(IV) as an intermediate has been decided by the addition of manganese(II) [16–20]. It is widely accepted that reduction proceeds *via* three consecutive one-electron steps in the presence of transition metal ions [1].

$$Cr^{VI} + M^{n+} \longrightarrow Cr^{V} + M^{(n+1)+} \qquad (1)$$

$$Cr^{V} + M^{n+} \longrightarrow Cr^{IV} + M^{(n+1)+} \qquad (2)$$

$$Cr^{IV} + M^{n+} \longrightarrow Cr^{III} + M^{(n+1)+} \qquad (3)$$

The existence of different chromium(VI) species in acid solutions, and the tendency of chromium(III) to form a variety of complexes, give systems of considerable complexity [21]. Therefore, different attempts have been made to confirm the intermediacy of chromium(IV) and chromium(V) by use of competitive experiments.

The kinetics of oxidation of some α-hydroxy acids (mandelic [12], lactic [22], glycolic [23], malic [24], tartaric [25] and citric [26]) by chromic acid have been reported in the presence of manganese(II). However, the details of manganese(II) oxidation by chromium(VI) are not yet known. A study of such a redox reaction should provide information relevant to the hypothesis previously advanced [14]. Our preliminary observations indicate that addition of traces of manganese(II) to a solution of chromium(VI) and EDTA enhances the absorbance of the reaction mixture at 500 nm significantly. It is interesting to find out how the oxidation occurs whenever the direct oxidation of manganese(II) by chromium(VI) is thermodynamically not feasible [13–14]. This paper deals with the oxidation of manganese(II) by chromium(VI) in the presence of EDTA.

Experimental

Materials

Ethylenediaminetetraacetic acid disodium salt (98%, s.d.fine, India), $MnCl_2$ (99%, Merck, India) and $K_2Cr_2O_7$ (99%, Merck, India) were used to prepare stock solutions. To maintain the [H^+] constant, $HClO_4$ (Fisher, 70%, reagent grade) was used. The solution of EDTA was stored in a polyethene bottle as its solution

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gradually leaches metal ions from glass containers, resulting in a change in the effective [EDTA]. The solution of $K_2Cr_2O_7$ was stored in a dark glass bottle. Doubly distilled (first from alkaline $KMnO_4$), deionized and CO_2-free H_2O was used as solvent.

Kinetic measurements

All kinetic measurements were carried out on a Bausch & Lomb Spectronic-20D Spectrophotometer. Known concentrations of EDTA and manganese(II) were mixed in a reaction vessel and a known concentration of chromium(VI) was stored in another vessel and thermostatted for a sufficient time to attain the desired temperature (±0.1 °C). The two solutions were then mixed and zero time was taken when half of the chromium(VI) solution had been added. The progress of the reaction was followed at 500 nm by monitoring the changes in absorbance. For this purpose, aliquots of the reaction mixture were removed at definite time intervals and cooled in an ice-bath to quench the reaction before each measurement. The *pseudo*-first-order rate constants (k_{obs}, s^{-1}) were determined from the linear part of the plots of log(absorbance) *versus* time.

Product identification

It is well known that the spectra of $K_2Cr_2O_7$ and the chromium(III)-EDTA complex solution possess a shoulder located at 425 nm [27] (Figure 1A) and two bands with λ_{max} = 410 and 550 nm [28] (Figure 1C), respectively. It is observed that the spectrum of $K_2Cr_2O_7$ changes upon the addition of a mixture of EDTA and manganese(II) solutions. The shoulder at 425 nm gradually disappears and two new bands start to appear at 500 and 725 nm (Figure 1B). It was also observed that the yellow reaction mixture became pink immediately in the presence of manganese(II). Thus, we conclude that the new spectrum (Figure 1B) is that of the manganese(III)-EDTA complex with λ_{max} = 500 nm [29, 30]. On the other hand, the band at 725 nm is assigned to the chromium(V)-EDTA complex [31]. After completion of the reaction, the u.v.–vis spectrum was also recorded. Our spectrum consists of two bands with λ_{max} = 400 and 550 nm (Figure 1C). The most characteristic part of the chromium(III) spectrum is the two d–d transitions observable in the 350–650 nm region [32]. Our λ_{max} values are in good agreement with the literature values [28, 29]. These results indicate that EDTA coordinates with the chromium(III) species. As the aqua chromium(III) ion is known to be inert towards ligand exchange [33], therefore, under our experimental conditions, the reduction product of chromium(VI) is the chromium(III)-EDTA complex (purple, λ_{max} = 400 and 550 nm).

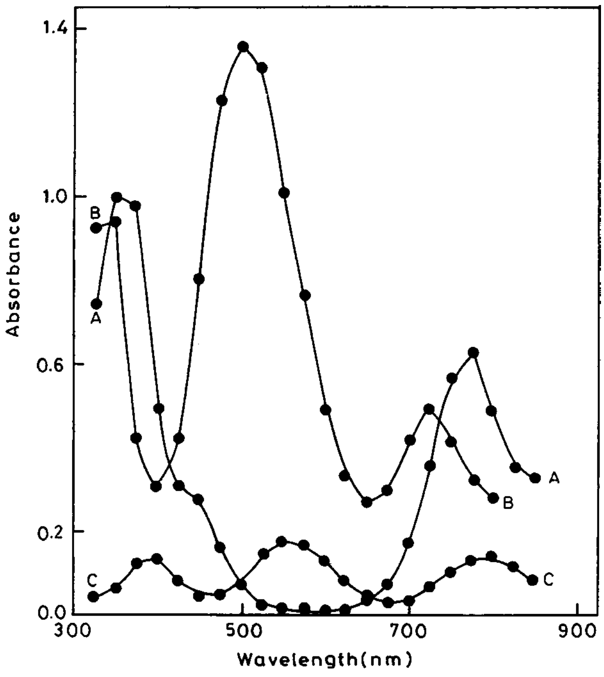


Fig. 1. U.v–vis spectra of mixtures at different time intervals and after completion of the reaction containing $[Cr^{VI}]$ = 5.0×10^{-4} mol dm^{-3}, [EDTA] = 14.0×10^{-3} mol dm^{-3} and $[Mn^{II}]$ = 16.0×10^{-3} mol dm^{-3} at 25 °C. *Reaction conditions:* no Mn(II) (A); Cr(VI) + EDTA + Mn(II) (B); and time 12 min(B) and 6 h (C).

Results and discussion

The most interesting features of the present observations are the decrease in the absorbance of the reaction mixture at 500 nm in the presence of $HClO_4$ and the vital role played by the order of mixing manganese(II) and $HClO_4$ in the formation of a pink species. The presence of acid also catalyses the oxidation of EDTA by chromium(VI) [34]. Therefore, the choice of the best conditions for the kinetic experiments is a crucial problem that we address first. In order to examine the effect of variables, experiments were tried at $[Cr^{VI}]$ (1.0–6.0×10^{-4} mol dm^{-3}), $[Mn^{II}]$ (4.0–20.0×10^{-3} mol dm^{-3}) and $HClO_4$ (4.6–23.3×10^{-2} mol dm^{-3}). It should also be emphasized here that reactions were studied without adding $HClO_4$.

Reaction in the absence of $HClO_4$

When chromium(VI) (5.0×10^{-4} mol dm^{-3}) was allowed to react with manganese(II) (4.0–20.0×10^{-3} mol dm^{-3}) in the presence of EDTA (20.0×10^{-3} mol dm^{-3}) at 25 °C, and the reaction was monitored spectrophotometrically, unusual kinetic behavior was observed (Figure 2). At 500 nm [λ_{max} manganese(III)], the absorbance first increased until it reached a maximum, then decreased with time. This behavior indicates the formation and disappearance of the manganese(III) during the course of reaction.

Oxidation of manganese(II) by chromium(VI) in the presence of EDTA has been studied kinetically as a function of [EDTA], $[Mn^{II}]$, $[Cr^{VI}]$ and temperature.

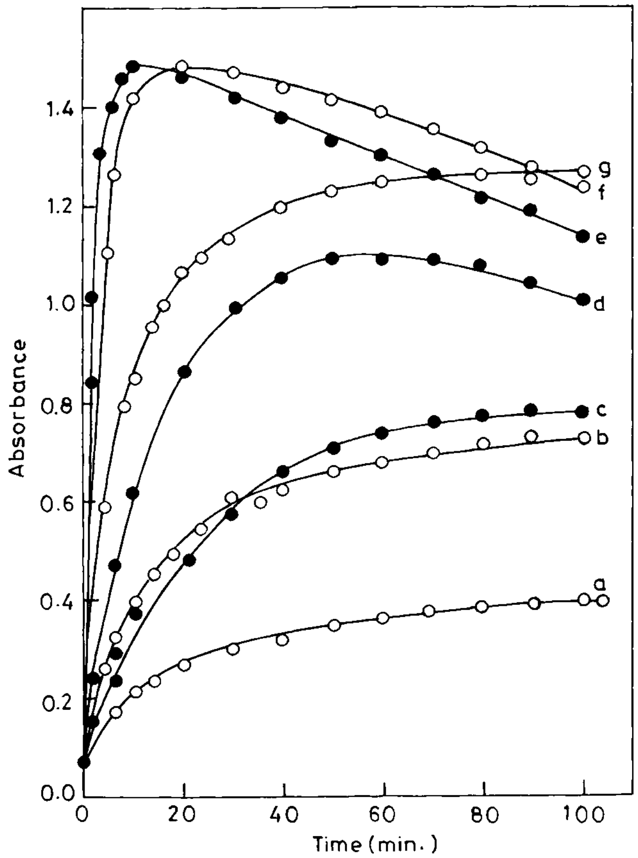


Fig. 2. Absorbance *versus* time plots as a function of [EDTA] (○) and $[Mn^{II}]$ (●) at 500 nm. *Reaction conditions:* 25 °C; $[Cr^{VI}] = 5.0 \times 10^{-4}$ mol dm^{-3}; [EDTA] = 1.6×10^{-3} mol dm^{-3} (a); 3.0×10^{-3} mol dm^{-3} (b); $[Mn^{II}] = 4.0 \times 10^{-3}$ mol dm^{-3} (c); 6.0×10^{-3} mol dm^{-3} (d) and 20.0×10^{-3} mol dm^{-3} (e); 16.0×10^{-3} mol dm^{-3} (f) and 5.0×10^{-3} mol dm^{-3} (g).

The results are compiled in Tables 1–3 and Figures 3–6. In the first set of experiments the reaction was studied as a function of $[Mn^{II}]$ ($4.0–20.0 \times 10^{-3}$ mol dm^{-3}) at constant [EDTA] (20.0×10^{-3} mol dm^{-3}), $[Cr^{VI}]$ (5.0×10^{-4} mol dm^{-3}) and temperature (25 °C). The values of k_{obs} increased with increase in $[Mn^{II}]$. A plot of k_{obs} *versus* $[Mn^{II}]$ is nonlinear passing through the origin (Figure 3A). However, a double logarithmic plot between k_{obs} and $[Mn^{II}]$ resulted in two straight lines with slopes = 1.0 and 3.0 (Figure 3B). The reaction follows different order kinetics with respect to $[Mn^{II}]$: it is third and first for the $[Mn^{II}]$ range $4–12.0 \times 10^{-3}$ and $12.0–20.0 \times 10^{-3}$ mol dm^{-3}, respectively. Figure 4 shows the effect of $[Mn^{II}]$ on the absorbance of formation of the manganese(III)-EDTA complex. The absorbance of the reaction mixture at 500 nm increases with $[Mn^{II}]$ from 4.0×10^{-3} to 20.0×10^{-3} mol dm^{-3}. At higher $[Mn^{II}]$ ($\geq 20.0 \times 10^{-3}$ mol dm^{-3}), there is no change in the absorbance. These findings indicate that the absorbance increases until $[Mn^{II}]$ becomes equal to [EDTA].

In the second set of experiments, the effect of [EDTA] on the k_{obs} was studied at constant $[Mn^{II}]$ (16.0×10^{-3} mol dm^{-3}), $[Cr^{VI}]$ (5.0×10^{-4} mol dm^{-3}) and temperature (25 °C). Variation of [EDTA] ($3.0–14.0 \times 10^{-3}$ mol dm^{-3}) increased the reaction rate (Table 1). The slope of the plot of log k_{obs} *versus* log[EDTA] was found to be 1.4. Therefore, the order in [EDTA] lies between first and second. On the other hand, [EDTA] has the same type of effect on the absorbance of the reaction mixture as that of $[Mn^{II}]$ (Figure 4). The invariance of rate constants over a variation in the initial $[Cr^{VI}]_T$ ($1.0–6.0 \times 10^{-4}$ mol dm^{-3}) at fixed $[Mn^{II}]$ (20.0×10^{-3} mol dm^{-3}), [EDTA] (20.0×10^{-3} mol dm^{-3}) and temperature (25 °C) is indicative of first-order dependence of the reaction in $[Cr^{VI}]_T$ (Table 1) and the total $[Cr^{VI}]$ must be used in the rate Equation, *i.e.*,

$$\text{d[coloured complex]/d}t = k_{obs}[Cr^{VI}]_T \qquad (4)$$

The reaction was also studied at 25, 30, 35, 40, 45 and 50 °C at constant $[Mn^{II}]$ (20.0×10^{-3} mol dm^{-3}), $[Cr^{VI}]$ (5.0×10^{-4} mol dm^{-3}) and [EDTA] (20.0×10^{-3} mol dm^{-3}). The values of k_{obs} as a function of temperature are given in Table 2. The Arrhenius plot of log k_{obs} *versus* 1/T was linear. The value of the activation energy (E_a) was calculated from the slope of the Arrhenius plot and was recorded along with other activation parameters ($\Delta H^{\#}, \Delta S^{\#}$) (Table 2).

From the experimental data, the total reaction may be written in two slow steps: Equations (5) and (6)

$$Cr^{IV} + 2\,EDTA + Mn^{II} \longrightarrow Cr^{III}\text{-}EDTA + Mn^{III} - EDTA \qquad (5)$$

$$Mn^{III}\text{-}EDTA \longrightarrow Mn^{II} + \text{ other products} \qquad (6)$$

The first step corresponds to the oxidation of manganese(II), whereas the second step corresponds to the reduction of manganese(III). These observations are in agreement with the results of Khan and Kabir-ud-Din [35], and Huber and Haight [11].

In aqueous solution, various chromium(VI) species exist in equilibrium. The nature of these species depends upon the pH and the concentration of potassium dichromate [36]. These species are designated as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-}, H_2CrO_4 and $HCrO_3^+$ [35]. In dilute solution (as in the present case) the monomeric form ($HCrO_4^-$) predominates. On the other hand, the EDTA also participates in acid-base equilibria and various species like H_6Y^{2+}, H_5Y^+, H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-} and Y^{4-} (Y = EDTA) exist in aqueous solution, as suggested by Underwood [37]. However, the species H_6Y^{2+}, H_5Y^+, H_4Y, H_3Y^-, HY^{3-} and Y^{4-} do not participate in the present reaction since we have not used $[H^+]$. Consequently, the major and reactive species of EDTA, *e.g.*, H_2Y^{2-}, would form a complex with manganese(II).

Taking into account the nature of the chromium(III) species, interestingly, it is to be noted that chro-

Table 1. Variation of rate constants on [EDTA], $[Mn^{II}]$ and $[Cr^{VI}]$ at 25 °C in the absence of $HClO_4$

10^3[EDTA] (mol dm^{-3})	$10^3[Mn^{II}]$ (mol dm^{-3})	$10^4[Cr^{VI}]$ (mol dm^{-3})	$10^3\ k^a_{obs}(s^{-1})$	$10^5\ k^b_{obs}\ (s^{-1})$
20.0	0.0	5.0	no reaction	no reaction
3.0	16.0	5.0	0.3	not observed
5.0			0.7	not observed
8.0			1.2	0.09
10.0			2.3	1.7
12.0			2.6	2.6
14.0			3.2	3.2
16.0			3.3	3.6
0.0	20.0	5.0	no reaction	no reaction
20.0	4.0	5.0	0.2	not observed
	6.0		0.4	not observed
	8.0		1.0	1.0
	10.0		2.4	1.9
	12.0		4.3	2.8
	14.0		5.4	3.3
	16.0		6.6	3.6
	18.0		7.2	3.7
	20.0		7.6	3.8
20.0	20.0	0.0	no reaction	no reaction
20.0	20.0	1.0	8.2	3.8
		2.0	8.1	3.8
		3.0	8.3	3.8
		4.0	8.0	3.8
		5.0	7.6	3.8
		6.0	7.8	3.8

[a] Formation and [b] decomposition of Mn^{III}-EDTA complex, respectively.

Table 2. Variation of rate constants on temperature and activation parameters in the absence of $HClO_4^a$

Temp.(°C)	$10^3\ k^b_{obs}(s^{-1})$	$10^5 k^c_{obs}(s^{-1})$
25	7.6	3.8
30	11.6	8.9
35	15.5	14.1
40	18.1	21.7
45	23.9	31.9
50	Very fast	51.8
Activation parameters		
E_a (kJ mol^{-1})	30	71
$\Delta H^{\#}$ (kJ mol^{-1})	28	68
$\Delta S^{\#}$ (J K^{-1} mol^{-1})	−200	−169

[a] $[Cr^{VI}] = 5.0 \times 10^{-4}$ mol dm^{-3}, [EDTA] $= 20.0 \times 10^{-3}$ mol dm^{-3} and $[Mn^{II}] = 20.0 \times 10^{-3}$ mol dm^{-3}; [b] Formation and [c] decomposition of Mn^{III}-EDTA complex, respectively.

Table 3. Dependence of rate constant on $[HClO_4]$

$10^2[HClO_4]^a$ (mol dm^{-3})	$10^4 k^b_{obs}(s^{-1})$	$10^5\ k^c_{obs}\ (s^{-1})$
0.0	76.7	3.8
4.6	40.9	7.6
9.2	17.6	21.7
13.9	1.9	30.7
18.5	0.09	not observed
23.2	not observed	not observed

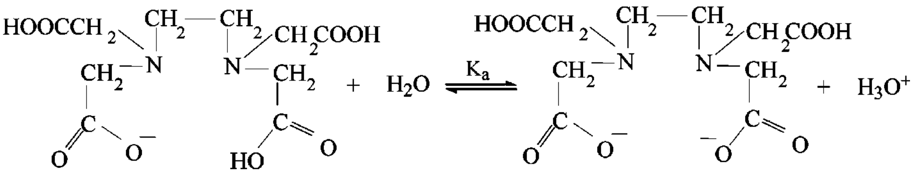
[a] $[Cr^{VI}] = 5.0 \times 10^{-4}$ mol dm^{-3}, [EDTA] $= 20.0 \times 10^{-3}$ mol dm^{-3}; $[Mn^{II}] = 20.0 \times 10^{-3}$ mol dm^{-3} and temperature = 25 °C; [b] Formation and [c] decomposition of Mn^{III}-EDTA complex, respectively.

mium(III) forms a complex with EDTA. Addition of EDTA to an authentic chromium(III) sample produced no change in the λ_{max} values for *ca.* 72 h in the absence of $[H^+]$. Thus, it is confirmed that EDTA must be present in the inner coordination sphere of a chromium ion with a valence higher than 3. On the other hand, EDTA also reacts with metal ions. The reaction with cations, *e.g.*, M^{2+}, may be written as

$$M^{2+} + H_2Y^{2-} \longrightarrow MY^{2-} + 2\ H^+ \qquad (7)$$

This equation indicates that there is always a competition in the solution between metal ions and hydrogen ions seeking the negative sites on EDTA [38].

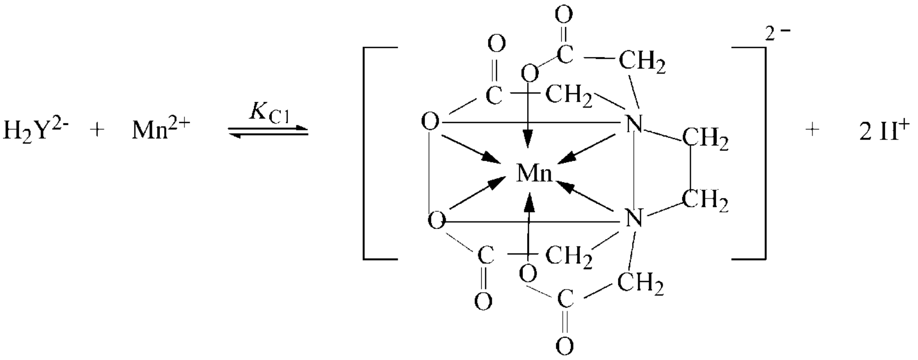
It is known that $Mn(H_2O)_6^{2+}$ will not reduce chromium(VI). Thus, we may safely conclude that chromium(VI)-EDTA and manganese(II)-EDTA complexes must be the only reactive species of chromium(VI) and manganese(II), respectively. Hence, the steps of the redox reaction can be written as shown in Scheme 1.



(H_3Y^-) (H_2Y^{2-})

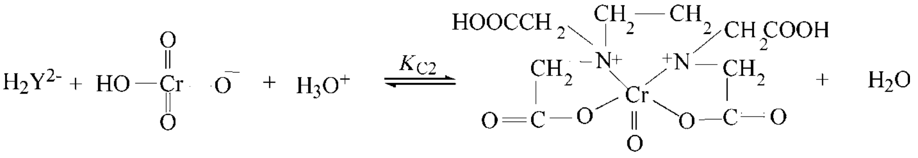
(8)

$$2HCrO_4^- \overset{K_{Cr}}{\rightleftharpoons} Cr_2O_7^{2-} + H_2O \tag{9}$$



(C1)

(10)



(C2)

(11)

$$C1 + C2 \overset{K_{OS}}{\rightleftharpoons} \underset{(OS)}{(C1)(C2)} \tag{12}$$

$$OS \xrightarrow{k_1} \underset{\lambda_{max} = 500\ nm}{Mn^{III}\text{-}EDTA} + \underset{\lambda_{max} = 725\ nm}{Cr^{V}\text{-}EDTA} \tag{13}$$

$$Cr^{V}\text{-}EDTA + C1 \xrightarrow{fast} Cr^{IV}\text{-}EDTA + Mn^{III}\text{-}EDTA \tag{14}$$

$$Cr^{IV}\text{-}EDTA + C1 \xrightarrow{fast} Cr^{III}\text{-}EDTA + Mn^{III}\text{-}EDTA \tag{15}$$

Scheme 1.

In Scheme 1, the reactive species of EDTA (H_2Y^{2-}) and Cr(VI) ($HCrO_4^-$) readily form complexes C1 and C2 with Mn^{II} and EDTA, respectively [Equations (10) and (11)]. However, the direct oxidation of C1 by C2 is not possible. Thus, the reaction may generally be expressed by Equation (12) (K_{os} is the rapid equilibrium for the encounter complex formation between the redox couple [39, 40]). By analogy with previous results [39, 40] we assume that OS decomposes in a rate-determining one-step one-electron oxidation-reduction mechanism to give manganese(III)-EDTA and chromium(V)-EDTA.

At constant [H^+], the value of the complex formation constant (K_{os}) was determined by using the relation (16) [41].

$$\frac{[Cr^{VI}]_T[EDTA][Mn^{II}]}{\Delta A} = \frac{[EDTA]\ or\ [Mn^{II}]}{\Delta\varepsilon l} + \frac{1}{K_{OS}\Delta\varepsilon l} \tag{16}$$

where $[Cr^{VI}]_T$ is the total metal ion concentration, ΔA the difference in absorbance between the complex and chromium(VI) at the wavelength 500 nm, $\Delta\varepsilon$ the difference in absorption coefficients and l the path length (1.0 cm). To test the validity of Equation (16), the left hand side term was plotted *versus* [EDTA] or [Mn^{II}] which was found to be fairly linear (Figure 5). From the

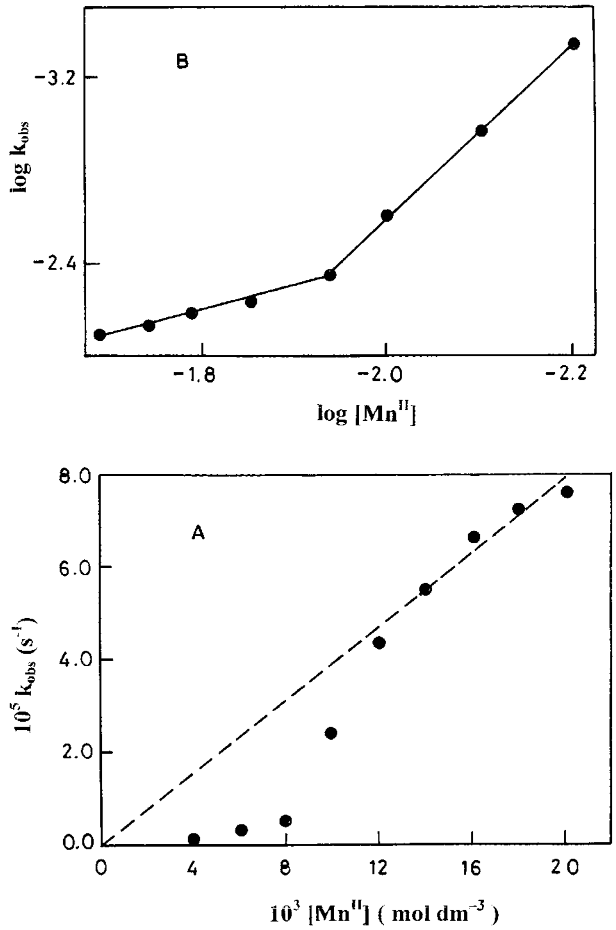


Fig. 3. (A) plot showing the effect of [Mn^{II}] on k_{obs}. (B) plot of log k_{obs} *versus* log [Mn^{II}]. *Reaction conditions:* 25 °C; [Cr^{VI}] = 5.0×10^{-4} mol dm^{-3} and [EDTA] = 20.0×10^{-3} mol dm^{-3}.

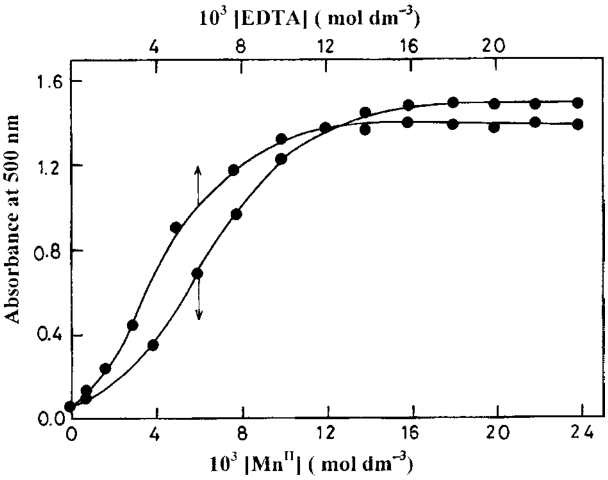


Fig. 4. Effect of [Mn^{II}] and [EDTA] on the absorbance (at 500 nm) of the formation of the Mn^{III}-EDTA complex. *Reaction conditions:* 25 °C; [Cr^{VI}] = 5.0×10^{-4} mol dm^{-3} ; after 12 min of mixing.

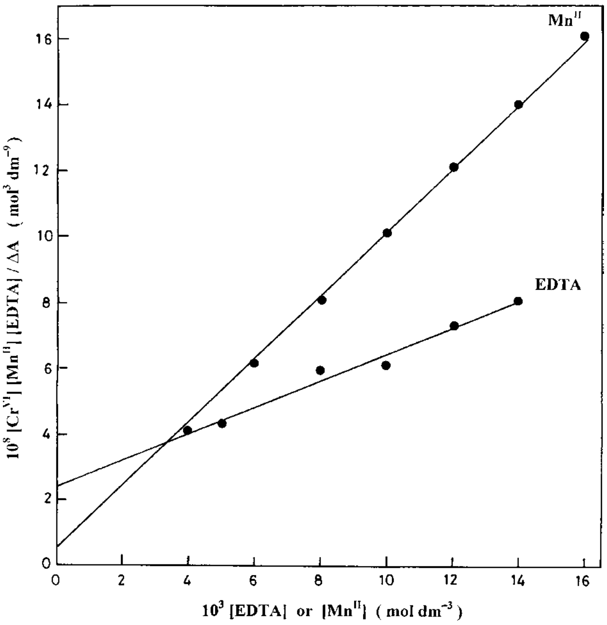


Fig. 5. Plots of the left-hand-side of Equation (16) *versus* [EDTA or Mn^{II}] at 25 °C and [Cr^{VI}] = 5.0×10^{-4} mol dm^{-3}.

slope and intercept, the values of K_{os} and $\Delta\varepsilon$ were calculated and found to be 1.75×10^2 and 2.4×10^5 mol^{-2} dm^6 for EDTA and 1.66×10^3 and 1.0×10^5 mol^{-2} dm^6 for manganese(II) variations.

A rate law consistent with Scheme 1 may be expressed as Equation (17) conforming to

$$V = d[\text{coloured complex}]/dt = \frac{k_1[Cr^{VI}]_T[Mn^{II}][EDTA]}{\{(1/K_{C2}K_{C1}[EDTA]) + 1\}} \tag{17}$$

and

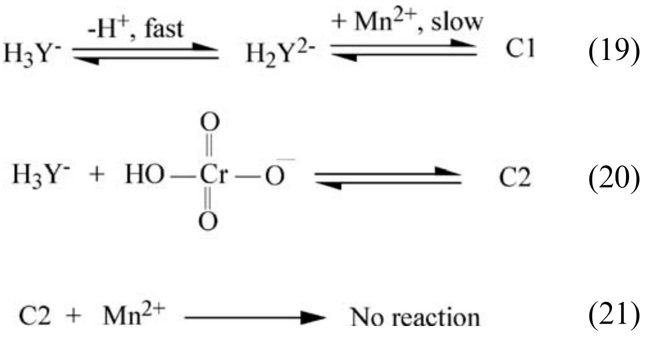
$$k_{obs} = \frac{k_1[Mn^{II}][EDTA]}{\{(1/K_{C2}K_{C1}[EDTA]) + 1\}} \tag{18}$$

the observed first-order behavior with respect to [Cr^{VI}].

Effect of [$HClO_4$] on reaction rate

In order to gain further insight into the mechanistic aspects and the role of hydrogen ion, a series of kinetic experiments were carried out at constant [Mn^{II}] (20.0×10^{-3} mol dm^{-3}), [Cr^{VI}] (5.0×10^{-4} mol dm^{-3}), [EDTA] (20.0×10^{-3} mol dm^{-3}) and temperature (25 °C). The rate of formation of the manganese(III)-EDTA complex decreased with the increase in [$HClO_4$], whereas its rate of decomposition increased with increase in [$HClO_4$] (Table 3). A quite noticeable effect can be observed for [$HClO_4$] $\geq 18.5 \times 10^{-2}$ mol dm^{-3}. As can be seen from Figure 6 (typical example), added $HClO_4$ inhibits the rate of formation. In order to ascertain whether $HClO_4$ is competing with manganese(II) in the oxidation, the reaction was conducted separately in the absence of manganese(II) under otherwise similar conditions. It was observed that the rate of oxidation was almost negligible in the absence of manganese(II).

In the presence of $HClO_4$, there is competition between H^+ and manganese(II) to react with the reactive species of EDTA. The unique role of the hydrogen ion can be explained by considering Equation (19) between EDTA, H^+ and manganese(II) (Scheme 2).



$$H_3Y^- \underset{}{\overset{-H^+,\ \text{fast}}{\rightleftharpoons}} H_2Y^{2-} \overset{+Mn^{2+},\ \text{slow}}{\rightleftharpoons} C1 \qquad (19)$$

$$H_3Y^- + HO{-}Cr(=O)_2{-}O^- \rightleftharpoons C2 \qquad (20)$$

$$C2 + Mn^{2+} \longrightarrow \text{No reaction} \qquad (21)$$

Scheme 2.

As the $[H^+]$ increases, the probability of C1 formation decreases; the equilibrium shifts towards the protonation of EDTA. The H_3Y species react with chromium(VI) to form an anhydride species, C2. Equation (21) suggests further that free manganese(II) ion cannot be oxidized by chromium(VI).

Kinetics of the decomposition of the manganese(III)-EDTA complex

The absorbance at 500 nm *versus* time plots (Figure 6) indicates that the reaction proceeds through the formation and decomposition of the manganese(III)-EDTA complex. It was noticed that the decomposition of this complex depends on the reaction conditions, *i.e.*, [EDTA], $[Mn^{II}]$, $[HClO_4]$ and temperature. The rate constants of the decomposition were determined from the slopes of plots of log(absorbance) *versus* time. These values are summarized in Tables 1–3. At constant $[Mn^{II}]$, $[Cr^{VI}]$ and temperature, the rate constant increased with the increase in [EDTA]. Likewise, at constant [EDTA], $[Cr^{VI}]$ and temperature, the rate constant increased with the increase in $[Mn^{II}]$. The decomposition was not observed at lower $[Mn^{II}]$ ($\leq 6.0 \times 10^{-3}$ mol dm^{-3}) as well as at lower [EDTA] ($\leq 5.0 \times 10^{-3}$ mol dm^{-3}) (Table 1). The *pseudo*-first-order rate constant remained unchanged with the increase in $[Cr^{VI}]$ (Table 1), showing first-order in $[Cr^{VI}]$. The k_{obs} values at different temperatures are given in Table 2. Using Arrhenius and Eyring equations, the activation parameters were calculated and presented in Table 2. The rate constant also increased with the increase in $[H^+]$ (Table 3). The double logarithmic plots of k_{obs} *versus* [EDTA], k_{obs} *versus* $[Mn^{II}]$ and k_{obs} *versus* $[H^+]$ gave straight lines with positive slopes (1.8, 2.4 and 1.1, respectively) showing second-, higher than second- and first-order dependence each on [EDTA], [Mn(II)] and $[H^+]$. Based on these findings and other results discussed earlier, the following mechanism (Scheme 3) is proposed.

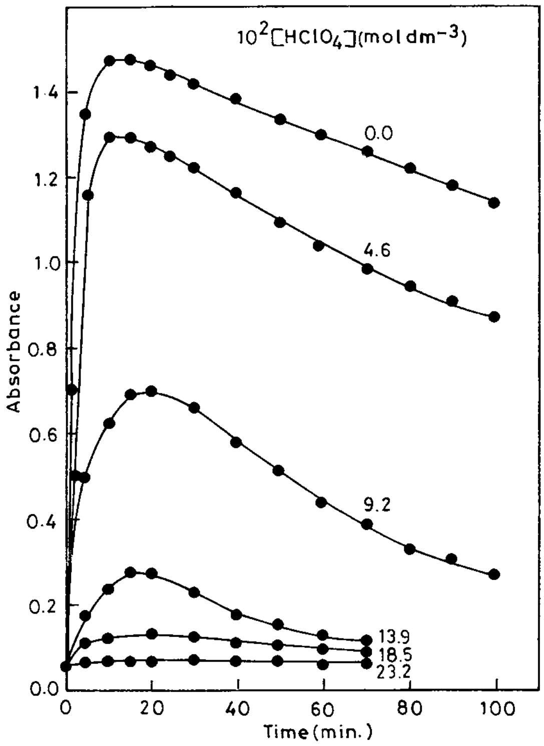


Fig. 6. Absorbance *versus* time plots at 500 nm. *Reaction conditions:* 25 °C; $[Cr^{VI}] = 5.0 \times 10^{-4}$ mol dm^{-3}, $[EDTA] = 20.0 \times 10^{-3}$ mol dm^{-3} and $[Mn^{II}] = 20.0 \times 10^{-3}$ mol dm^{-3}.

$$Mn^{III}\text{-EDTA} + \underset{(H_3Y^-)}{\text{EDTA}} \overset{K_{es}}{\rightleftharpoons} \text{complex} \qquad (22)$$

$$\text{complex} + Mn^{III}\text{-EDTA} \longrightarrow 2Mn^{II}\text{-EDTA} + \text{oxidation products} \qquad (23)$$

Scheme 3.

Conclusions

The most interesting feature of this study is the reduction of chromium(VI) by manganese(II) in the presence of EDTA. We are unaware of any precedence in the redox chemistry of this system. The reducing nature may be explained by the outer-sphere complexation between chromium(VI)-EDTA and manganese(II)-EDTA complexes (Scheme 1); this type of behavior is rare in the redox reactions involving intermolecular electron transfer from the chelated reductant to the chelated oxidant.

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