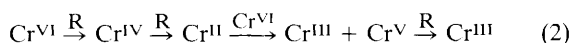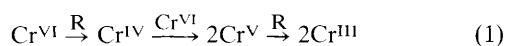# Evidence for the Involvement of Chromium(II) as an Intermediate in the Reduction of Chromium(VI) to Chromium(III) by Formaldehyde

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The reaction between chromium(VI) and formaldehyde in aqueous perchloric acid is inhibited by manganese(II) ion, according to the relation $k_1 = a/(1 + b[Mn^{2+}]) + c$; manganese(II) ion and formaldehyde compete to reduce the intermediate Cr^{IV}, and Cr^{II} is an intermediate.

According to Westheimer's mechanisms,[1,2] there are in principle two possibilities for the reduction of Cr^{VI} to Cr^{III} by two-equivalent reducing agents (R), one involving only Cr^V and Cr^{IV} as intermediates [eqn. (1)], and the other involving also Cr^{II} as intermediate [eqn. (2)].

$$Cr^{VI} \xrightarrow{R} Cr^{IV} \xrightarrow{Cr^{VI}} 2Cr^V \xrightarrow{R} 2Cr^{III} \qquad (1)$$

$$Cr^{VI} \xrightarrow{R} Cr^{IV} \xrightarrow{R} Cr^{II} \xrightarrow{Cr^{VI}} Cr^{III} + Cr^V \xrightarrow{R} Cr^{III} \qquad (2)$$

In contrast to the opinion of most authors, who prefer mechanism (1) over mechanism (2) on the grounds that Cr^{II} is such a powerful reducing agent that it is not considered a likely species in the system,[3] Beattie and Haight have pointed out that mechanism (2) has not been ruled out by any valid experiment or theoretical argument, since the reaction $Cr^{IV} + 2e^- \rightarrow Cr^{II}$ has an extremely favourable reduction potential.[4]

Since the problem of the general mechanism for the reduction of chromium(VI) by two-equivalent reducing agents [mechanism (1) vs. (2)] has not been definitively resolved, and also since there is a growing interest in the reduction mechanisms of chromium(VI) because it is a powerful carcinogen,[5,6] we report now experimental results indicating that the reduction of Cr^{VI} to Cr^{III} by formaldehyde in aqueous perchloric acid takes place via mechanism (2), and not via mechanism (1).

The experiments were done under pseudo-first-order conditions (large excess of reductant with respect to oxidant), and the kinetic runs were followed by measuring the absor-

bance of hydrogenchromate ion at 352 nm ($\varepsilon = 1.556 \times 10^3$ dm^3 mol^{-1} cm^{-1})[7] with a Varian Cary 219 UV–VIS spectrophotometer. The first-order rate constants (k_1) were obtained from the ln ($A - A_\infty$) vs. time linear plots (average linear correlation coefficient 0.999981). Two independent determinations were done for each k_1 value (average standard deviation $\pm 0.9\%$ for a total of 300 experiments).

Manganese(II) ion is known to have an inhibiting effect on the reactions of chromium(VI) with many reductants (for instance, with formaldehyde[8]). Our results indicate that this effect can be conveniently described by a function of the type in eqn. (3), where a, b and c are fitting parameters. Parameter b can be optimized so that the k_1 vs. $1/(1 + b[Mn^{2+}])$ plots are linear (Fig. 1), and is a measure of the inhibition of the Cr^{VI}–HCHO reaction by manganese(II). It is practically independent of the initial chromium(VI) concentration, but is inversely proportional to the formaldehyde concentration, since the experimental data obtained can be fitted to eqn. (4) (Fig. 2). It is widely accepted[9] that the inhibition effect of manganese(II) ion on oxidations by chromium(VI) is due to trapping of the intermediate Cr^{IV} according to eqn. (5).

$$k_1 = a/(1 + b[Mn^{2+}]) + c \qquad (3)$$

$$b = -(203 \pm 1120) + (1.03 \pm 0.06) \times 10^3/[HCHO] \qquad (4)$$

$$Cr^{IV} + Mn^{2+} \rightarrow Cr^{III} + Mn^{3+} \qquad (5)$$
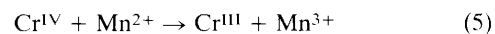
Thus, both mechanisms (1) and (2) are consistent in principle with the inhibition by Mn^{2+}, since its reaction with

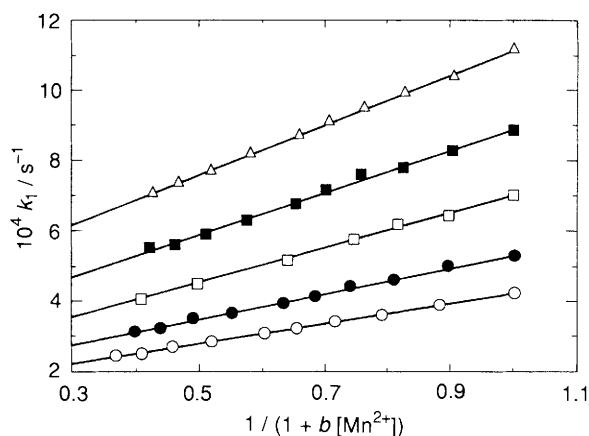**Fig. 1** Dependence of the first-order rate constant on the concentration of manganese(II) ion. $[Cr^{VI}]_0 = 8.01 \times 10^{-4}$, $[HCHO] = 0.133$, $[HClO_4] = 0.146$, $[MnSO_4] = 0$–2.73×10^{-4} mol dm^{-3}, $T/^{\circ}C = 14.8$ (○), 19.9 (●), 24.9 (□), 30.3 (■) and 35.2 (△).

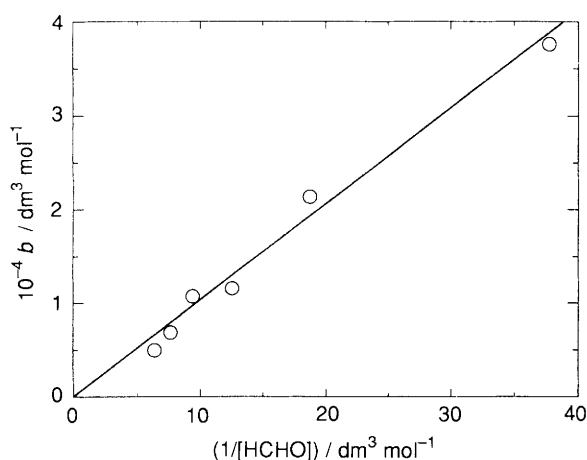**Fig. 2** Dependence of parameter b on the reductant concentration. $[Cr^{VI}]_0 = 8.01 \times 10^{-4}$, $[HCHO] = 2.66 \times 10^{-2}$–$0.160$, $[HClO_4] = 0.146$, $[MnSO_4] = 0$–4.01×10^{-4} mol dm^{-3}, $T/^{\circ}C = 25.0$.

Cr^{IV} in each case avoids the intervention in the reaction sequence of a second Cr^{VI}. However, our results indicate that Mn^{2+} is competing with the reductant (R) and not with Cr^{VI} for reaction with Cr^{IV}, since parameter b decreases with increasing [HCHO] (Fig. 2) whereas it is independent of $[Cr^{VI}]_0$. Therefore, those results are consistent with mechanism (2) and not with mechanism (1). We can thus conclude that Cr^{II} is actually involved as an intermediate in the reduction of Cr^{VI} to Cr^{III} by formaldehyde.

A more quantitative analysis can be done by application of the steady-state approximation. It is easy to demonstrate that both mechanisms (1) and (2) lead then to dependences of k_1 on [Mn^{2+}] formally identical to equation (3), but the expressions obtained for parameter b are different. Effectively, by application of the steady-state approximation to the intermediate Cr^{IV}, we obtain eqns. (6)–(10) for mechanism (1) in the presence of manganese(II) ion.

$$r = -d[Cr^{VI}]/dt = (k_{fs}[R] + k_{ox}[Cr^{IV}])[Cr^{VI}] \quad (6)$$

$$k_1 = r/[Cr^{VI}] = k_{fs}[R] + k_{ox}[Cr^{IV}] \quad (7)$$

$$[Cr^{IV}] = k_{fs}[Cr^{VI}][R]/(k_{ox}[Cr^{VI}] + k_{inh}[Mn^{2+}]) \quad (8)$$

$$k_1 = \{k_{ox}[Cr^{VI}]/(k_{ox}[Cr^{VI}] + k_{inh}[Mn^{2+}]) + 1\}k_{fs}[R]$$

$$= \{1/(1 + k_{inh}[Mn^{2+}]/k_{ox}[Cr^{VI}]) + 1\}k_{fs}[R] \quad (9)$$
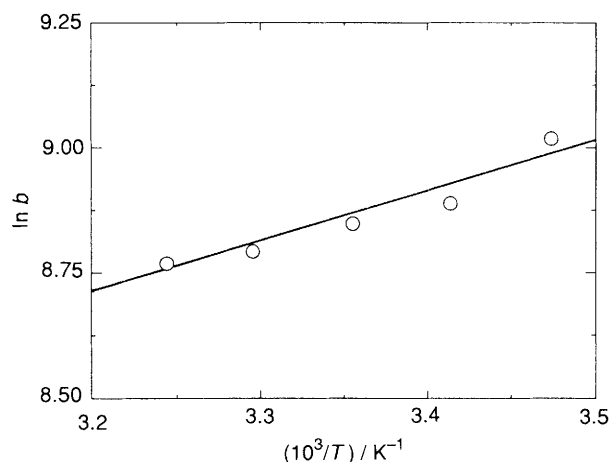
$$b = k_{inh}/k_{ox}[Cr^{VI}] \quad (10)$$

Fig. 3 Dependence of parameter b on temperature. $[Cr^{VI}]_0 = 8.01 \times 10^{-4}$, $[HCHO] = 0.133$, $[HClO_4] = 0.146$, $[MnSO_4] = 0$–2.73×10^{-4} mol dm^{-3}, $T/^{\circ}C = 14.8$–35.2.

On the other hand, by application of the steady-state approximation to the intermediates Cr^{II} and Cr^{IV}, we obtain eqns. (11)–(16) for mechanism (2) in the presence of manganese(II) ion.

$$r = -d[Cr^{VI}]/dt = (k_{fs}[R] + k'_{ox}[Cr^{II}])[Cr^{VI}] \quad (11)$$

$$k_1 = r/[Cr^{VI}] = k_{fs}[R] + k'_{ox}[Cr^{II}] \quad (12)$$

$$[Cr^{II}] = k_{red}[Cr^{IV}][R]/k'_{ox}[Cr^{VI}] \quad (13)$$

$$[Cr^{IV}] = k_{fs}[Cr^{VI}][R]/k_{red}[R] + k_{inh}[Mn^{2+}]) \quad (14)$$

$$k_1 = \{k_{red}[R]/(k_{red}[R] + k_{inh}[Mn^{2+}]) + 1\}k_{fs}[R]$$

$$= \{1/(1 + k_{inh}[Mn^{2+}]/k_{red}[R]) + 1\}k_{fs}[R] \quad (15)$$

$$b = k_{inh}/k_{red}[R] \quad (16)$$

In eqns. (6)–(16), k_{fs} is the rate constant corresponding to the reaction between Cr^{VI} and R [first step of mechanisms (1) and (2)], whereas k_{inh}, k_{ox} and k_{red} are the rate constants for the reactions of the intermediate Cr^{IV} with the inhibitor Mn^{2+} (eqn. (5)], with the oxidizing agent Cr^{VI} [mechanism (1)] and with the reducing agent R [mechanism (2)], respectively, and k'_{ox} is the rate constant for the reaction between the intermediate Cr^{II} and the oxidant Cr^{VI} [mechanism (2)].

Our results are consistent with eqn. (16) and not with eqn. (10); *i.e.* mechanism (2) is the correct one.

We have also studied the effect of temperature on parameter b, the corresponding Arrhenius plot (Fig. 3) leading to the conclusion that the difference between the activation energies associated with rate constants k_{inh} and k_{red} is given by eqn. (17). Therefore, the activation energy for the reaction Cr^{IV}–HCHO is a little higher than that for the reaction Cr^{IV}–Mn^{2+} [eqn. (5)].

$$E_{a,inh} - E_{a,red} = -8.6 \pm 1.4 \text{ kJ mol}^{-1} \quad (17)$$

For the oxidation of aldehydes by chromium(VI) in aqueous acidic media, a third mechanism has been proposed[10] which resembles mechanism (2), the main difference being that the reaction between Cr^{IV} and R is a one-electron redox step (instead of a two-electron one), so that Cr^{III} and an organic free radical would be formed, the latter being oxidized by chromium(VI) in a later step. This mechanism would be in agreement both with the inhibition effect of Mn^{2+} on the Cr^{VI}–HCHO reaction and with the decrease of the inhibition as the reductant concentration increases [see eqn. (4)].

However, Scott and coworkers[11] in recent work have developed several methods for the preparation of Cr^{IV} by reaction of Cr^{2+} with several oxidants in aqueous perchloric acid solution, and they have reported that the reduction of Cr^{IV} to Cr^{II} by methanol in aqueous acid solution is thermodynamically more favourable than its reduction to

Cr^{III}, since the favourable reduction potential for $Cr^{IV} \rightarrow Cr^{III}$ is offset by the largely unfavourable potential for the oxidation of methanol to an unstable free radical ($\cdot CH_2OH$). We think that this argument might also be applied to our case, leading to the conclusion that the reaction between the intermediate Cr^{IV} and formaldehyde is a two-electron redox step [as proposed in mechanism (2)], since a one-electron step would lead to the formation of an unstable organic free radical ($HCO^\cdot$).

To the best of our knowledge, this is the first evidence for the involvement of Cr^{II} as an intermediate in the reduction of Cr^{VI} to Cr^{III}. Work is in progress to decide whether other two-equivalent reducing agents react with chromium(VI) as formaldehyde does. Preliminary results seem to indicate that the oxidations of both formic acid and propan-2-ol by chromium(VI) also take place through mechanism (2) and not mechanism (1). Thus, the conclusions now reported might be of general applicability.

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