

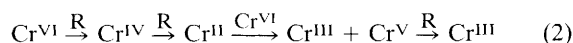
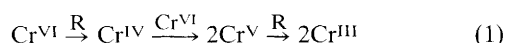
## Evidence for the Involvement of Chromium(II) as an Intermediate in the Reduction of Chromium(VI) to Chromium(III) by Formaldehyde

Joaquin F. Perez-Benito,\* Conchita Arias and Driss Lamrhari

*Departamento de Quimica Fisica, Facultad de Quimica, Universidad de Barcelona, Marti i Franques, 1, 08028 Barcelona, Spain*

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

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



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

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,<sup>5,6</sup> we report now experimental results indicating that the reduction of  $\text{Cr}^{\text{VI}}$  to  $\text{Cr}^{\text{III}}$  by formaldehyde in aqueous perchloric acid takes place *via* mechanism (2), and not *via* mechanism (1).

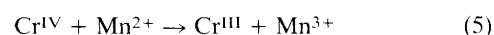
The experiments were done under pseudo-first-order conditions (large excess of reductant with respect to oxidant), and the kinetic runs were followed by measuring the absor-

bance of hydrogenchromate ion at 352 nm ( $\epsilon = 1.556 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )<sup>7</sup> 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).

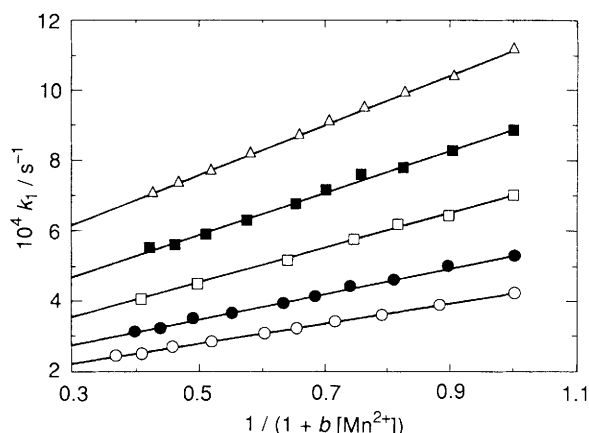
Manganese(II) ion is known to have an inhibiting effect on the reactions of chromium(VI) with many reductants (for instance, with formaldehyde<sup>8</sup>). Our results indicate that this effect can be conveniently described by a function of the type in eqn. (3), where  $a$ ,  $b$  and  $c$  are fitting parameters. Parameter  $b$  can be optimized so that the  $k_1$  vs.  $1/(1 + b[\text{Mn}^{2+}])$  plots are linear (Fig. 1), and is a measure of the inhibition of the  $\text{Cr}^{\text{VI}}$ -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<sup>9</sup> that the inhibition effect of manganese(II) ion on oxidations by chromium(VI) is due to trapping of the intermediate  $\text{Cr}^{\text{IV}}$  according to eqn. (5).

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

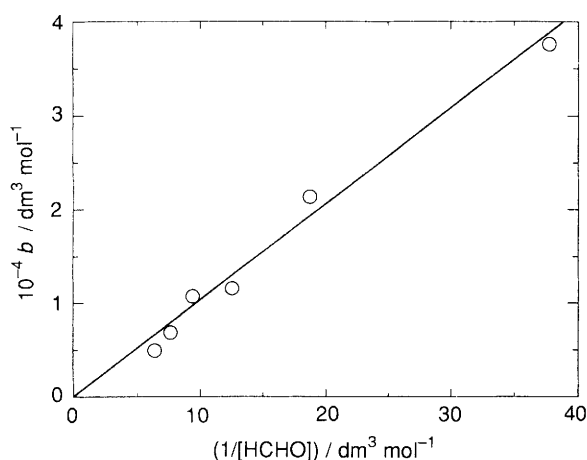
$$b = -(203 \pm 1120) + (1.03 \pm 0.06) \times 10^3/[\text{HCHO}] \quad (4)$$



Thus, both mechanisms (1) and (2) are consistent in principle with the inhibition by  $\text{Mn}^{2+}$ , since its reaction with



**Fig. 1** Dependence of the first-order rate constant on the concentration of manganese(II) ion.  $[\text{Cr}^{\text{VI}}]_0 = 8.01 \times 10^{-4}$ ,  $[\text{HCHO}] = 0.133$ ,  $[\text{HClO}_4] = 0.146$ ,  $[\text{MnSO}_4] = 0-2.73 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $T/^\circ\text{C} = 14.8$  (○), 19.9 (●), 24.9 (□), 30.3 (■) and 35.2 (△).



**Fig. 2** Dependence of parameter  $b$  on the reductant concentration.  $[\text{Cr}^{\text{VI}}]_0 = 8.01 \times 10^{-4}$ ,  $[\text{HCHO}] = 2.66 \times 10^{-2}-0.160$ ,  $[\text{HClO}_4] = 0.146$ ,  $[\text{MnSO}_4] = 0-4.01 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $T/^\circ\text{C} = 25.0$ .

$\text{Cr}^{\text{IV}}$  in each case avoids the intervention in the reaction sequence of a second  $\text{Cr}^{\text{VI}}$ . However, our results indicate that  $\text{Mn}^{2+}$  is competing with the reductant (R) and not with  $\text{Cr}^{\text{VI}}$  for reaction with  $\text{Cr}^{\text{IV}}$ , since parameter  $b$  decreases with increasing  $[\text{HCHO}]$  (Fig. 2) whereas it is independent of  $[\text{Cr}^{\text{VI}}]_0$ . Therefore, those results are consistent with mechanism (2) and not with mechanism (1). We can thus conclude that  $\text{Cr}^{\text{II}}$  is actually involved as an intermediate in the reduction of  $\text{Cr}^{\text{VI}}$  to  $\text{Cr}^{\text{III}}$  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  $[\text{Mn}^{2+}]$  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  $\text{Cr}^{\text{IV}}$ , we obtain eqns. (6)–(10) for mechanism (1) in the presence of manganese(II) ion.

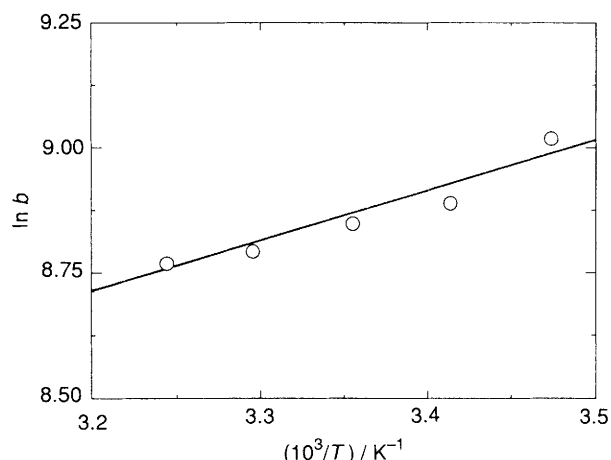
$$r = -d[\text{Cr}^{\text{VI}}]/dt = (k_{\text{fs}}[\text{R}] + k_{\text{ox}}[\text{Cr}^{\text{IV}}])[\text{Cr}^{\text{VI}}] \quad (6)$$

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

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

$$k_1 = \{k_{\text{ox}}[\text{Cr}^{\text{VI}}]/(k_{\text{ox}}[\text{Cr}^{\text{VI}}] + k_{\text{inh}}[\text{Mn}^{2+}]) + 1\}k_{\text{fs}}[\text{R}] \quad (9)$$

$$b = k_{\text{inh}}/k_{\text{ox}}[\text{Cr}^{\text{VI}}] \quad (10)$$



**Fig. 3** Dependence of parameter  $b$  on temperature.  $[\text{Cr}^{\text{VI}}]_0 = 8.01 \times 10^{-4}$ ,  $[\text{HCHO}] = 0.133$ ,  $[\text{HClO}_4] = 0.146$ ,  $[\text{MnSO}_4] = 0-2.73 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $T/^\circ\text{C} = 14.8-35.2$ .

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

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

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

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

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

$$k_1 = \{k_{\text{red}}[\text{R}]/(k_{\text{red}}[\text{R}] + k_{\text{inh}}[\text{Mn}^{2+}]) + 1\}k_{\text{fs}}[\text{R}] \quad (15)$$

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

In eqns. (6)–(16),  $k_{\text{fs}}$  is the rate constant corresponding to the reaction between  $\text{Cr}^{\text{VI}}$  and R [first step of mechanisms (1) and (2)], whereas  $k_{\text{inh}}$ ,  $k_{\text{ox}}$  and  $k_{\text{red}}$  are the rate constants for the reactions of the intermediate  $\text{Cr}^{\text{IV}}$  with the inhibitor  $\text{Mn}^{2+}$  (eqn. (5)), with the oxidizing agent  $\text{Cr}^{\text{VI}}$  [mechanism (1)] and with the reducing agent R [mechanism (2)], respectively, and  $k'_{\text{ox}}$  is the rate constant for the reaction between the intermediate  $\text{Cr}^{\text{II}}$  and the oxidant  $\text{Cr}^{\text{VI}}$  [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  $k_{\text{inh}}$  and  $k_{\text{red}}$  is given by eqn. (17). Therefore, the activation energy for the reaction  $\text{Cr}^{\text{IV}}-\text{HCHO}$  is a little higher than that for the reaction  $\text{Cr}^{\text{IV}}-\text{Mn}^{2+}$  [eqn. (5)].

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

For the oxidation of aldehydes by chromium(vi) in aqueous acidic media, a third mechanism has been proposed<sup>10</sup> which resembles mechanism (2), the main difference being that the reaction between  $\text{Cr}^{\text{IV}}$  and R is a one-electron redox step (instead of a two-electron one), so that  $\text{Cr}^{\text{III}}$  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  $\text{Mn}^{2+}$  on the  $\text{Cr}^{\text{VI}}-\text{HCHO}$  reaction and with the decrease of the inhibition as the reductant concentration increases [see eqn. (4)].

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

$\text{Cr}^{\text{III}}$ , since the favourable reduction potential for  $\text{Cr}^{\text{IV}} \rightarrow \text{Cr}^{\text{III}}$  is offset by the largely unfavourable potential for the oxidation of methanol to an unstable free radical ( $\cdot\text{CH}_2\text{OH}$ ). We think that this argument might also be applied to our case, leading to the conclusion that the reaction between the intermediate  $\text{Cr}^{\text{IV}}$  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 ( $\text{HCO}\cdot$ ).

To the best of our knowledge, this is the first evidence for the involvement of  $\text{Cr}^{\text{II}}$  as an intermediate in the reduction of  $\text{Cr}^{\text{VI}}$  to  $\text{Cr}^{\text{III}}$ . 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.

Received, 25th October 1991; Com. 1/05447C

## References

- 1 F. H. Westheimer, *Chem. Rev.*, 1949, **45**, 419.
- 2 W. Watanabe and F. H. Westheimer, *J. Chem. Phys.*, 1949, **17**, 61.
- 3 R. Stewart, *Oxidation Mechanisms*, Benjamin, New York, 1964, p. 37.
- 4 J. K. Beattie and G. P. Haight, in *Inorganic Reaction Mechanisms*, ed. J. O. Edwards, Wiley, New York, 1972, Part II, p. 96.
- 5 P. H. Connert and K. E. Wetterhahn, *J. Am. Chem. Soc.*, 1985, **107**, 4282.
- 6 S. L. Brauer and K. E. Wetterhahn, *J. Am. Chem. Soc.*, 1991, **113**, 3001.
- 7 M. J. Burkhardt and R. C. Thompson, *J. Am. Chem. Soc.*, 1972, **94**, 2999.
- 8 A. C. Chatterji and S. K. Mukherjee, *J. Am. Chem. Soc.*, 1958, **80**, 3600.
- 9 G. P. Haight, T. J. Huang and B. Z. Shkhashiri, *J. Inorg. Nucl. Chem.*, 1971, **33**, 2169.
- 10 J. March, *Advanced Organic Chemistry. Reactions, Mechanisms and Structure*, Wiley, New York, 1985, p. 630.
- 11 S. L. Scott, A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1991, **113**, 7787.