Long-lived intermediates in the reduction of chromium(VI) by D-ribose†

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One of the reaction pathways in the reduction of chromium(VI) by D-ribose in aqueous perchloric acid follows the sequence Cr(VI) → $\mathbf{I_a}$ → $\mathbf{I_b}$ → Cr(III), where $\mathbf{I_a}$ and $\mathbf{I_b}$ are long-lived intermediates. A kinetic study of the reactivity of those intermediates with different substances revealed that $\mathbf{I_a}$ is a complex of Cr(IV) with D-ribose (or one of its partially oxidized forms), whereas $\mathbf{I_b}$ is a complex of Cr(II) with an organic free radical. The formation of the latter suggests that in the reduction of the intermediate Cr(IV) by the organic substrate both hydride-ion transfer and hydrogen-atom transfer are involved.

In the course of a study on the reduction of chromium(VI) by D-ribose in acidic media,[1] two long-lived intermediates were detected. Since it has been reported that ribonucleotides (but not deoxyribonucleotides) slowly reduce Cr(VI) to Cr(V) at physiological pH,[2] the study of these intermediates might be of some interest to enhance our knowledge of the mechanism involved in the expression of the well-known toxic and carcinogenic effects of chromate.[3–5] The present kinetic study throws some light on both the nature and reactivity of these intermediates.

Experimental

Materials and methods

The inorganic compounds were purchased from Merck and the organic ones from Sigma–Aldrich. The solvent was water previously subjected to three consecutive purification steps: deionization, distillation and circulation through a Millipore system. The kinetic runs were monitored by periodic measurement of the solution absorbance in a thermostatted quartz cell with a Shimadzu UV-160 A spectrophotometer. In total, 846 experiments were done.

Preparation of intermediate $\mathbf{I_a}$

An aqueous mixture containing Cr(VI) (1.54×10^{-3} M), D-ribose (3.08×10^{-2} M) and $HClO_4$ (0.731 M) was thermostatted at 30.0 °C and the progress of the reaction was monitored spectrophotometrically. After 84 min the spectrophotometer data indicated that the Cr(VI) had been completely reduced, and all the chromium was present as either the long-lived intermediate $\mathbf{I_a}$ or as the inert product Cr(III). Then, 10 cm^3 of the solution were mixed with 10 cm^3 of a thermostatted aqueous solution containing the additives necessary for each experiment, and the formation of the intermediate $\mathbf{I_b}$ from $\mathbf{I_a}$ under different experimental conditions was followed at 297 nm.

Preparation of intermediate $\mathbf{I_b}$

The reacting mixture was prepared as explained above for $\mathbf{I_a}$, but this time the reaction was allowed to progress until the absorbance at 297 nm reached a maximum. This happened 19.5 h after the beginning of the reaction, and at that moment the chromium was present in three forms: the long-lived intermediates $\mathbf{I_a}$ and $\mathbf{I_b}$ (the latter in its highest concentration) and the product Cr(III). Then, the necessary additives were added [Mn(II) was used in most experiments to trap the remaining intermediate $\mathbf{I_a}$], and the disappearance of $\mathbf{I_b}$ under different experimental conditions was followed at 297 nm.

Kinetic data

The absorbance *vs.* time couples for the beginning of each kinetic run were fitted by a nonlinear least-squares method to the equation:

$$A = a + bt + ct^2 \tag{1}$$

and an apparent value v'_0 of the initial rate (directly proportional to the true initial rate, v_0) was obtained as the absolute value of parameter b:

$$v'_0 = \left| \left(\frac{\mathrm{d}A}{\mathrm{d}t} \right)_{t=0} \right| = |b| = \varepsilon_{297} l v_0 \tag{2}$$

where ε_{297} is the molar absorption coefficient of the intermediate $\mathbf{I_b}$ at 297 nm (unknown quantity) and $l = 1$ cm is the optical pathlength. For each experiment, the apparent initial rate of disappearance of either $\mathbf{I_a}$ ($v'_{0,\mathrm{a}}$) or $\mathbf{I_b}$ ($v'_{0,\mathrm{b}}$) was obtained. In the first case, monitoring the formation of $\mathbf{I_b}$ from $\mathbf{I_a}$, the value of parameter b was >0. In the second case, monitoring the disappearance of $\mathbf{I_b}$, the value of b was <0.

Results

The intermediate $\mathbf{I_a}$ could be detected only by difference spectroscopy, using as a reference the same reacting mixture as that contained in the reaction cell but in the presence of concentrated $MnSO_4$, added at the beginning of the Cr(VI)/D-ribose reaction to suppress the formation of the long-lived intermediates. Under those conditions, the intermediate $\mathbf{I_a}$ showed a weak absorption band at 253 nm. The intermediate $\mathbf{I_b}$ could be detected by ordinary spectroscopy because of its strong band at 297 nm.

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† Electronic supplementary information (ESI) available: Figures showing the kinetic effects provoked by 2-propanol, *tert*-butanol, $HgCl_2$, $MnSO_4$, H_3PO_4, $CoSO_4$, L-ascorbic acid, $CuSO_4$, $Na_4P_2O_7$ and $FeSO_4$. See http://www.rsc.org/suppdata/nj/b0/b006827f/

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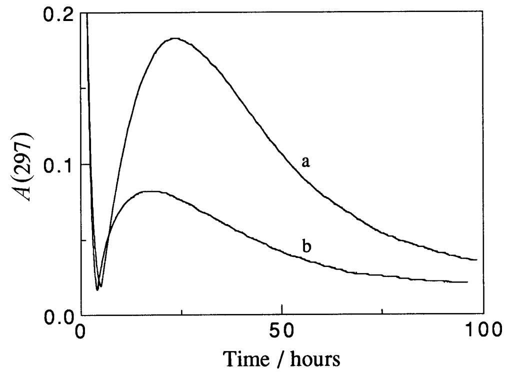

Fig. 1 Variation of the absorbance at 297 nm with time during the course of the reaction between Cr(VI) (7.68×10^{-4} M) and D-ribose (2.77×10^{-2} M) in the presence of $HClO_4$ (0.366 M) at 30.0 °C. $[MnSO_4] = 0$ (a) and 1.09×10^{-3} M (b).

In the curves shown in Fig. 1 the fast decrease of absorbance at the beginning of the reaction corresponds to the reduction of Cr(VI) to the intermediate $\mathbf{I_a}$. Once Cr(VI) is absent from the system, the intermediate $\mathbf{I_a}$ is slowly converted into the intermediate $\mathbf{I_b}$. From these kinetic plots it can be inferred that the ε values of Cr(VI) and $\mathbf{I_b}$ at 297 nm are both higher than that of $\mathbf{I_a}$.

Formation of intermediate $\mathbf{I_b}$ from $\mathbf{I_a}$

The initial rate of formation of $\mathbf{I_b}$ from $\mathbf{I_a}$ (expressed as $v'_{0,\mathrm{a}}$) and the maximum concentration reached for $\mathbf{I_b}$ [expressed as the maximum absorbance at 297 nm, $A(297)_{\max}$] were directly proportional to the initial concentration of $\mathbf{I_a}$ (order $= 1.05 \pm 0.04$, from a log $v'_{0,\mathrm{a}}$ *vs.* log $[\mathbf{I_a}]_0$ plot), whereas they were only slightly affected by the concentration of D-ribose (order $= 0.008 \pm 0.012$), as seen from Fig. 2.

The reaction showed acid catalysis approaching a saturation limit at high $[H^+]$, so that $[H^+]/v'_{0,\mathrm{a}}$ increased linearly with $[H^+]$ (Fig. 3). The maximum concentration of $\mathbf{I_b}$ changed with $[H^+]$ according to a parabolic profile. Both $v'_{0,\mathrm{a}}$ and $A(297)_{\max}$ decreased when the ionic strength was increased by addition of $NaClO_4$, the slope of a log $v'_{0,\mathrm{a}}$ *vs.* $\sqrt{I}/(1+\sqrt{I})$ plot being $-0.51 \pm 0.14\ M^{-1/2}$.

Both $v'_{0,\mathrm{a}}$ and $A(297)_{\max}$ increased with temperature. The activation energy obtained from an Arrhenius plot for the former is 93.0 ± 1.5 kJ mol^{-1} (Fig. 4).

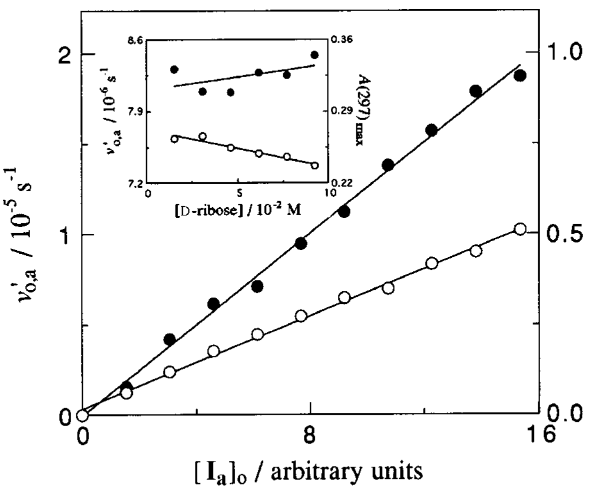

Fig. 2 Dependencies of $v'_{0,\mathrm{a}}$ (●) and the maximum absorbance at 297 nm (○) on the initial concentrations of $\mathbf{I_a}$ (main figure, [D-ribose] $= 3.08 \times 10^{-2}$ M, $[HClO_4] = 0.731$ M) and D-ribose (inset, $[HClO_4] = 0.366$ M) at 30.0 °C.

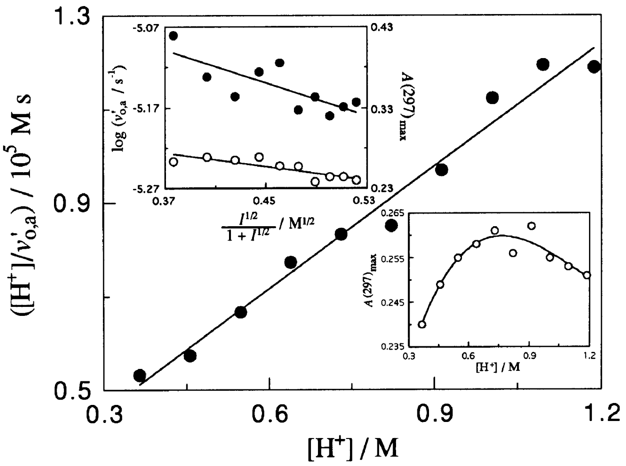

Fig. 3 Dependencies of $v'_{0,\mathrm{a}}$ (●) and the maximum absorbance at 297 nm (○) on the concentration of $HClO_4$ (main figure and lower inset, $[HClO_4] + [NaClO_4] = 1.19$ M) and the ionic strength (upper inset, $[HClO_4] = 0.366$ M) at [D-ribose] $= 1.54 \times 10^{-2}$ M and 30.0 °C.

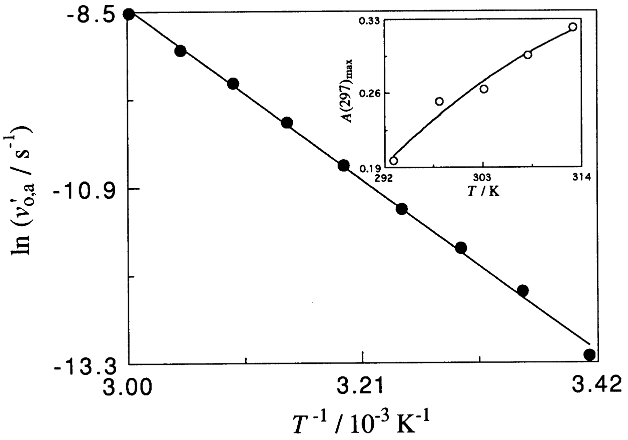

Fig. 4 Dependencies of $v'_{0,\mathrm{a}}$ (●) and the maximum absorbance at 297 nm (○) on temperature at [D-ribose] $= 1.54 \times 10^{-2}$ M and $[HClO_4] = 0.366$ M.

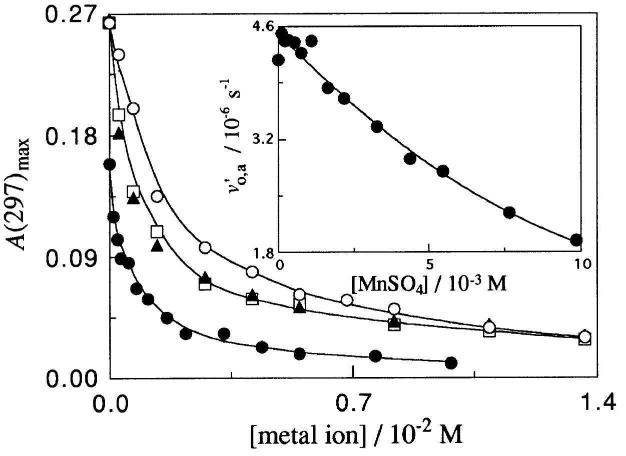

Fig. 5 Dependencies of the maximum absorbance at 297 nm (main figure) and $v'_{0,\mathrm{a}}$ (inset) on the concentrations of Mn^{2+} (●, □, ▲) and Ce^{3+} (○) at [D-ribose] $= 1.54 \times 10^{-2}$ M (●, □, ○) or 3.08×10^{-2} M (▲), $[HClO_4] = 0.366$ M and 30.0 °C. The metal ion was added either at the beginning of the reaction (●) or at the instant when all the Cr(VI) was reduced (□, ▲, ○).

As shown in Fig. 5 the value of $A(297)_{max}$ decreased dramatically when either Mn^{2+} or Ce^{3+} was added. The effect was observed when the metal ion was added either at the beginning of the Cr(VI)/D-ribose reaction or at the instant when all the Cr(VI) had been reduced (*i.e.*, when the absorbance at 297 nm showed a minimum). The effect was independent of the concentration of D-ribose, and slightly more pronounced for Mn^{2+} than for Ce^{3+}. The value of $v'_{0,a}$ was affected (decreased) only when the metal ion was added at the beginning of the Cr(VI)/D-ribose reaction.

Addition of *tert*-butanol resulted in a parabolic profile of the $A(297)_{max}$ *vs.* [alcohol] plot, whereas the value of $v'_{0,a}$ did not change appreciably. Addition of 2-propanol resulted in a decrease of the value of $A(297)_{max}$, whereas the value of $v'_{0,a}$ increased.

Addition of Fe^{3+} resulted in a dramatic decrease of both $A(297)_{max}$ and $v'_{0,a}$. Addition of $[Fe(CN)_6]^{3-}$ resulted in an increase of $A(297)_{max}$ at low concentrations and in a decrease of $A(297)_{max}$ at high concentrations, whereas $v'_{0,a}$ was only slightly affected. However, addition of $CuSO_4$ resulted in an increase of $A(297)_{max}$, and $v'_{0,a}$ was not affected (Fig. 6).

The values of $v'_{0,a}$ and $A(297)_{max}$ were not appreciably affected by addition of 2-ethyl-2-hydroxybutyric acid (up to 5.95×10^{-3} M).

Reactivity of intermediate $\mathbf{I_b}$

The intermediate $\mathbf{I_b}$ was oxidized very rapidly by Tl^{3+} and, under stoichiometric conditions, the reaction followed second-order kinetics (Fig. 7). The amounts of different strong oxidants required to destroy a given amount of $\mathbf{I_b}$ and the corresponding second-order rate constants are compared in Table 1.

The intermediate $\mathbf{I_b}$ reacted more slowly with Hg^{2+}, with the rate *vs.* concentration plot showing a saturation limit, suggesting the probable formation of a complex between the reactants.

In the absence of Mn^{2+}, the intermediate $\mathbf{I_b}$ did not react at an appreciable rate with the reductants sulfite ion (up to 9.85×10^{-5} M) and L-cysteine (up to 1.67×10^{-3} M).

Decomposition of intermediate $\mathbf{I_b}$ in the presence of Mn(II)

In some experiments, in order to trap the remaining intermediate $\mathbf{I_a}$, Mn^{2+} was added when the intermediate $\mathbf{I_b}$ reached its maximum concentration. The increasing effect of the trapping agent on $v'_{0,b}$ (due to the sudden end to the formation of $\mathbf{I_b}$ from $\mathbf{I_a}$) was very pronounced at low $[Mn^{2+}]$, whereas $v'_{0,b}$ increased more slowly at high $[Mn^{2+}]$ (the ionic strength was kept constant, $[MnSO_4] + [ZnSO_4] = 0.500$ M). In the presence of Mn^{2+}, the decomposition of $\mathbf{I_b}$ was slightly autocatalytic, since in most experiments the rate did not decrease appreciably even when a considerable fraction of the intermediate had already disappeared. The decomposition of $\mathbf{I_b}$ was very slow in the absence of Mn^{2+} but much faster in its presence.

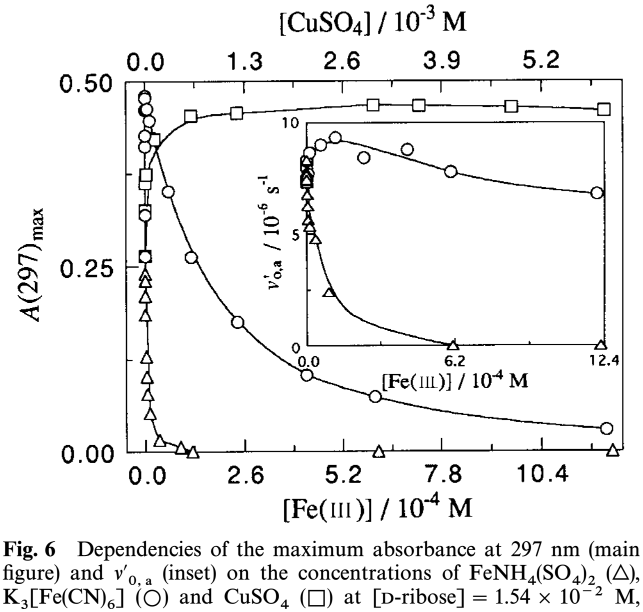

Fig. 6 Dependencies of the maximum absorbance at 297 nm (main figure) and $v'_{0,a}$ (inset) on the concentrations of $FeNH_4(SO_4)_2$ (△), $K_3[Fe(CN)_6]$ (○) and $CuSO_4$ (□) at [D-ribose] $= 1.54 \times 10^{-2}$ M, $[HClO_4] = 0.366$ M and 30.0 °C.

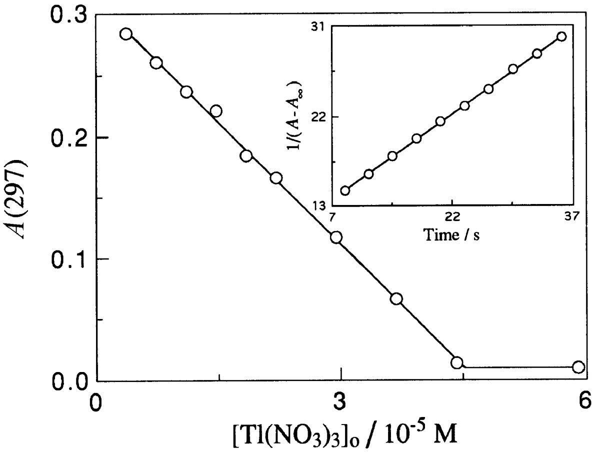

Fig. 7 Dependence of the final absorbance at 297 nm on the initial concentration of Tl^{3+} for a fixed initial concentration of intermediate $\mathbf{I_b}$ at [D-ribose] $= 1.54 \times 10^{-2}$ M, $[HClO_4] = 0.366$ M and 30.0 °C. Inset: Second-order kinetic plot for the reaction of intermediate $\mathbf{I_b}$ with Mn(III) under stoichiometric conditions at $[Na_4P_2O_7] = 2.88 \times 10^{-2}$ M, [D-ribose] $= 1.54 \times 10^{-2}$ M, $[HClO_4] = 0.535$ M and 15.6 °C.

The rate of decomposition of $\mathbf{I_b}$ in the presence of Mn^{2+} was independent of the concentration of D-ribose (order $= 0.02 \pm 0.03$, Table 2). The reaction was also insensitive to addition of $NaClO_4$ to change the ionic strength, but it showed base catalysis, since it was retarded by an increase of the concentration of $HClO_4$ (order $= -0.24 \pm 0.03$, Table 3).

The value of $v'_{0,b}$ increased with $[\mathbf{I_b}]_0$ (apparent order $= 1.66 \pm 0.06$) and followed an Arrhenius behavior (see

Table 1 Amounts of different oxidants required to reduce the intermediate $\mathbf{I_b}$ coming from 100 mmol of Cr(VI), and second-order rate constants for the reactions of $\mathbf{I_b}$ with these oxidants[a]

Oxidant	n_{ox}/mmol	$k_2/10^4$ M^{-1} s^{-1}
Tl^{3+}	5.89	>4[b]
MnO_4^-	6.34	>4[b]
Mn^{3+}	7.07	0.11[c]
Cr(VI)	7.35	0.07[b]
Ce^{4+}	10.8	>4[b]

[a] [D-ribose] $= 1.54 \times 10^{-2}$ M. [b] $[HClO_4] = 0.366$ M, 30.0 °C. [c] $[Na_4P_2O_7] = 2.88 \times 10^{-2}$ M, $[HClO_4] = 0.535$ M, 15.6 °C.

Table 2 Dependence of $v'_{0,b}$ on the concentration of D-ribose[a]

[D-ribose]/10^{-2} M	$v'_{0,b}/10^{-4}$ s^{-1}
1.54	5.14
3.08	4.67
4.62	4.79
6.15	4.99
7.69	5.20
9.23	5.26

[a] $[MnSO_4] = 0.250$ M, $[HClO_4] = 0.366$ M, 30.0 °C.

Table 3 Dependence of $v'_{0,\,b}$ on the concentrations of $NaClO_4$ and $HClO_4$[a]

$[NaClO_4]$/M	$[HClO_4]$/M	$v'_{0,\,b}/10^{-4}\ s^{-1}$
0.000	0.366[b]	5.14
0.091	0.366[b]	4.99
0.183	0.366[b]	4.90
0.274	0.366[b]	5.02
0.366	0.366[b]	5.11
0.457	0.366[b,c]	5.05
0.366	0.457[c]	4.61
0.274	0.548[c]	4.49
0.183	0.640[c]	4.43
0.091	0.731[c]	4.28
0.000	0.822[c]	4.05

[a] [D-ribose] = 1.54 × 10^{-2} M, $[MnSO_4]$ = 0.250 M, 30.0 °C. [b] Variable ionic strength. [c] Constant ionic strength ($[NaClO_4] + [HClO_4]$ = 0.822 M).

Fig. 8), the activation energy being 54.5 ± 1.3 kJ mol^{-1}. Dissolved oxygen had a remarkable accelerating effect on the decomposition of $\mathbf{I_b}$.

The reaction was catalyzed by L-cysteine and Fe^{3+} and, less efficiently, by HCO_2H (Fig. 9).

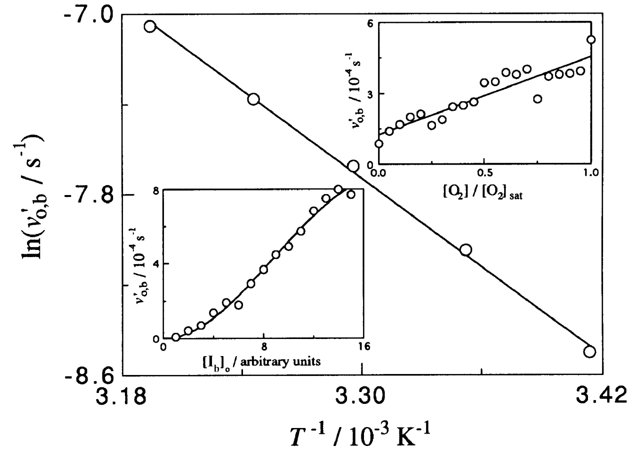

Fig. 8 Dependence of $v'_{0,\,b}$ on the temperature (main figure, [D-ribose] = 1.54 × 10^{-2} M, $[HClO_4]$ = 0.366 M), the initial concentration of $\mathbf{I_b}$ (lower inset, [D-ribose] = 2.31 × 10^{-2} M, $[HClO_4]$ = 0.548 M, 30.0 °C) and the concentration of O_2 (expressed as the ratio with respect to an air-saturated solution, upper plot, [D-ribose] = 1.54 × 10^{-2} M, $[HClO_4]$ = 0.366 M, 30.0 °C) in the presence of $MnSO_4$ (0.250 M).

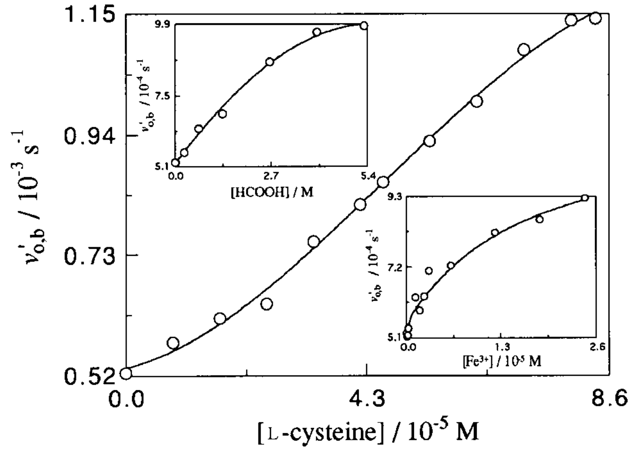

Fig. 9 Dependence of $v'_{0,\,b}$ on the concentrations of L-cysteine (main figure), formic acid (upper inset) and $FeNH_4(SO_4)_2$ (lower inset) at [D-ribose] = 1.54 × 10^{-2} M, $[MnSO_4]$ = 0.250 M, $[HClO_4]$ = 0.366 M and 30.0 °C.

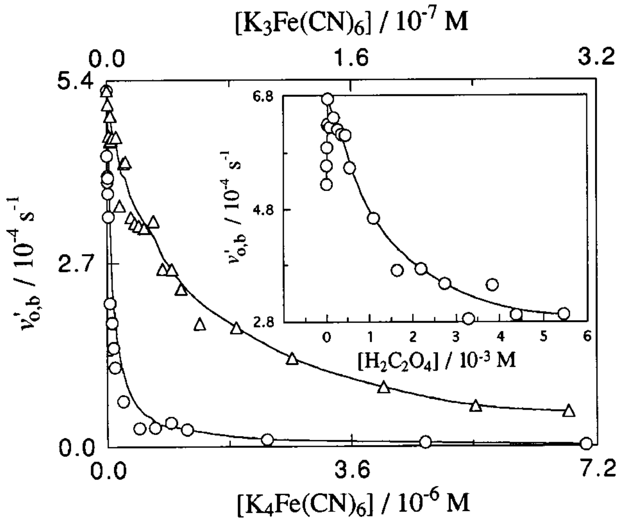

Fig. 10 Dependence of $v'_{0,\,b}$ on the concentrations of $K_4[Fe(CN)_6]$ (○), $K_3[Fe(CN)_6]$ (△) and oxalic acid (inset) at [D-ribose] = 1.54 × 10^{-2} M, $[MnSO_4]$ = 0.250 M, $[HClO_4]$ = 0.366 M and 30.0 °C.

The reaction was inhibited weakly by *tert*-butanol, $CoSO_4$ and H_3PO_4, and more strongly by $Na_4P_2O_7$, $CuSO_4$, $FeSO_4$ and L-ascorbic acid, but the most efficient inhibitors found were $K_3[Fe(CN)_6]$ and $K_4[Fe(CN)_6]$ (Fig. 10). The efficiencies of the different inhibitors are compared in Table 4. The inhibition by $CoSO_4$ was studied at constant ionic strength ($[CoSO_4] + [ZnSO_4]$ = 0.250 M).

Table 4 Concentrations of various inhibitors required to provoke a 5% decrease in $v'_{0,\,b}$[a]

Inhibitor	[Inhibitor]/M
$K_4[Fe(CN)_6]$	3.22 × 10^{-9}
$K_3[Fe(CN)_6]$	5.94 × 10^{-9}
L-Ascorbic acid	4.55 × 10^{-7}
$FeSO_4$	5.24 × 10^{-7}
$CuSO_4$	1.67 × 10^{-6}
$Na_4P_2O_7$	1.76 × 10^{-5}
H_3PO_4	9.73 × 10^{-3}
$CoSO_4$	8.25 × 10^{-2}
tert-Butanol	0.404

[a] [D-ribose] = 1.54 × 10^{-2} M, $[MnSO_4]$ = 0.250 M, $[HClO_4]$ = 0.366 M, 30.0 °C.

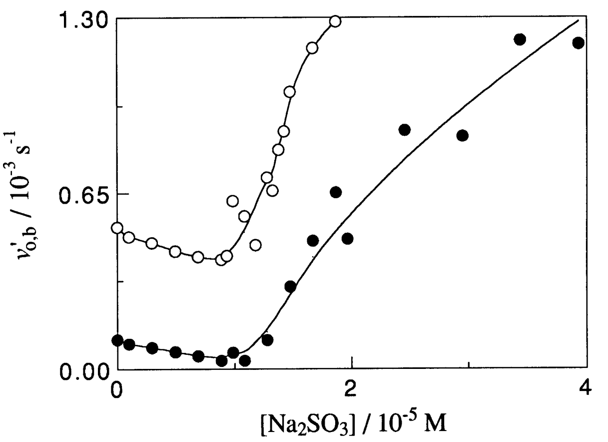

Fig. 11 Dependence of $v'_{0,\,b}$ on the concentration of Na_2SO_3 in the absence (○) and presence (●) of $Na_4P_2O_7$ (6.21 × 10^{-3} M) at [D-ribose] = 1.54 × 10^{-2} M, $[MnSO_4]$ = 0.250 M, $[HClO_4]$ = 0.366 M and 30.0 °C.

Oxalic acid behaved as a catalyst at low concentrations and as an inhibitor at high concentrations (Fig. 10, inset), whereas Na_2SO_3 behaved conversely, being an inhibitor at low concentrations and a catalyst at high concentrations (Fig. 11).

D-Mannitol (up to 4.08×10^{-2} M), 2-propanol (up to 3.27 M) and superoxide dismutase (up to 3.30×10^4 units per litre) had no appreciable effect on the decomposition of $\mathbf{I_b}$ in the presence of Mn^{2+}. The effect of acrylamide (up to 6.97×10^{-3} M) was also negligible, and no precipitation was observed upon addition of methanol.

Discussion

Intermediate $\mathbf{I_a}$

Manganese(II) and cerium(III) are very efficient trapping agents for the Cr(IV) formed as an intermediate in the reactions of Cr(VI) with most reductants.[6] The finding that addition of Mn^{2+} at the beginning of the Cr(VI)/D-ribose reaction (see Fig. 5) suppressed the formation of the two long-lived intermediates indicates that the first-formed intermediate, $\mathbf{I_a}$, is either Cr(IV) or some species formed from it. Since both Mn^{2+} and Ce^{3+} retained their power to suppress the formation of $\mathbf{I_b}$ if they were added at the instant of complete Cr(VI) reduction (when $\mathbf{I_a}$ reached its maximum concentration), the intermediate $\mathbf{I_a}$ must be either Cr(IV) or one of its precursors, but not one of its derivatives. Considering that most organic substrates reduce Cr(VI) directly to Cr(IV),[7] the only possible precursor to Cr(IV) would be a complex between Cr(VI) and the organic substrate. However, the UV-Vis spectrum of $\mathbf{I_a}$ is not consistent with a Cr(VI) complex.

Once established that the intermediate $\mathbf{I_a}$ is a form of Cr(IV), it must be explained why it behaves as a long-lived intermediate in these reacting media, considering that in the form of CrO^{2+} it is relatively short-lived (half-life of 0.75 min at room temperature in the absence of reducing agents).[8] Some experimental findings suggest that it is stabilized by complexation with at least one molecule of organic substrate (probably a partially oxidized form of D-ribose) as ligand, and that the latter acts as the electron donor in an internal redox process for the conversion of $\mathbf{I_a}$ into $\mathbf{I_b}$ without intervention of free molecules of D-ribose as reductant. These findings are the following: (i) The formation of $\mathbf{I_b}$ from $\mathbf{I_a}$ was of zero order in the concentration of free D-ribose (Fig. 2). (ii) The decreasing effect of added Mn^{2+} on the value of $A(297)_{max}$ was independent of the concentration of D-ribose, indicating that Mn^{2+} did not compete with the free molecules of D-ribose to trap Cr(IV). (iii) The absence of any effect of 2-ethyl-2-hydroxybutyric acid, an efficient stabilizing ligand for Cr(IV).[9] (iv) It has been reported that a dimeric form of Cr(III), including two molecules of D-ribose and another two molecules of oxidized D-ribose as ligands, is one of the reaction products from the reduction of Cr(VI) by D-ribose.[10]

Intermediate $\mathbf{I_b}$

The fact that $\mathbf{I_b}$ begins to be formed from $\mathbf{I_a}$ only when Cr(VI) has been completely reduced by D-ribose suggests that $\mathbf{I_b}$ is either Cr(II) or one of its derivatives. In this way, the rapid reoxidation of Cr(II) by Cr(VI)[11] would explain the inhibition provoked by the latter on the formation of $\mathbf{I_b}$. The formation of Cr(II) from $\mathbf{I_a}$, Cr(IV), would be the consequence of an internal 2-electron reduction of the latter by its organic ligand. That the intermediate $\mathbf{I_b}$ might be Cr^{2+} can be excluded in view that its high reducing character[12,13] would make its detection in O_2-containing solutions impossible for periods as long as the ones observed in these reacting systems (several days in the absence of Mn^{2+}).

Three of the possible derivatives that might be formed in the reacting system from Cr(II) are superoxochromium(III) ion ($CrOO^{2+}$), formed from the addition reaction of Cr^{2+} with O_2,[12,13] and two dimeric forms of Cr(III), $[CrOCr]^{4+}$ and $[Cr(OH)_2Cr]^{4+}$, the first dimer being formed from the addition reaction of Cr(IV) (as CrO^{2+}) with Cr^{2+} and the second dimer from the addition reaction of the first dimer with a molecule of water.[14]

By analogy with the 290 nm band in the UV spectrum of $CrOO^{2+}$, the band of intermediate $\mathbf{I_b}$ at 297 nm might have ligand-to-metal charge transfer character, although the absence in its UV spectrum of a band at 245 nm indicates that $\mathbf{I_b}$ is not a superoxide.[15] This conclusion is confirmed by the finding that the instability of intermediate $\mathbf{I_b}$ increased dramatically in the presence of O_2, whereas for $CrOO^{2+}$ the opposite happens.[7,16]

The intermediate $\mathbf{I_b}$ has a reducing character because it reacts very rapidly with many oxidants. This clearly indicates that $\mathbf{I_b}$ is not a dimeric form of Cr(III) either, since the latter are rather inert as reductants.[11]

The experimental results found in this work are consistent with the intermediate $\mathbf{I_b}$ being a complex between Cr(II) and a radical derived from a partially oxidized form of D-ribose. This complex may be denoted as CrR^{2+}. The reasons supporting this hypothesis are given below.

(i) The band in the UV spectrum of $\mathbf{I_b}$ at 297 nm is within the range observed (220–310 nm) for the highest absorption band in complexes of the type CrR^{2+} involving different organic radicals.[17]

(ii) Several substances act as catalysts in the decomposition of $\mathbf{I_b}$, whereas many others act as inhibitors, and some substances (such as oxalic acid and sulfite ion) even play both roles (catalysts and inhibitors). These findings suggest that the decomposition of $\mathbf{I_b}$ is a chain reaction: the catalysts might act through a promotion of the initiation step and the inhibitors through a promotion of the termination step. The decomposition of a complex of the type CrR^{2+}, with $R = CH(CH_3)_2$, in O_2-containing aqueous solutions is known to also be a chain reaction.[18,19]

(iii) The inhibiting effect on the decomposition of $\mathbf{I_b}$ caused by *tert*-butanol cannot be regarded as a solvent effect (provoked by a change in the medium dielectric constant) because no effect was found when an even higher concentration of 2-propanol was used. Instead, the inhibition is probably a consequence of the trapping of free radicals by the *tert*-butanol.[20] This again suggests that the decomposition of $\mathbf{I_b}$ occurs through a chain reaction with free radicals as the main chain carriers. Certainly, the absence of any noticeable effect of acrylamide seems contradictory with a chain reaction. However, since many other results are best explained by a chain mechanism, we favor this hypothesis over other explanations. In fact, the negative result with acrylamide might be due to some steric hindrance in the addition of the bulky organic free radicals derived from D-ribose to the double bond.

(iv) The decomposition of $\mathbf{I_b}$ was strongly inhibited by Fe^{2+} and Cu^{2+}. Similar effects of these ions on the decomposition of a CrR^{2+} complex have been reported.[18] The Cu^{2+} ions are efficient oxidants for organic free radicals.[21,22]

(v) The intermediate $\mathbf{I_b}$ reacted with both Hg^{2+} and Tl^{3+}. This agrees with the behavior reported for complexes of the type CrR^{2+}.[23–26]

(vi) The reactivity exhibited by the intermediate $\mathbf{I_b}$ toward several strong oxidants is consistent with the reactions reported between complexes of the type CrR^{2+} and some oxidizing agents.[27]

Mechanism

A reaction sequence explaining the formation of the two long-lived intermediates, and consistent with the kinetic data reported in a previous work on the Cr(VI)/D-ribose reaction,[1] as well as with those found in the present work, is shown in reactions (3)–(9)

$$C_5H_{10}O_5 + H_2CrO_4 \rightleftarrows C_5H_9O_4\text{–O–}CrO_3H + H_2O \quad (3)$$

$$C_5H_9O_4\text{–O–}CrO_3H + H^+ \rightleftarrows C_5H_9O_4\text{–O–}CrO_3H_2{}^+ \quad (4)$$

$$C_5H_9O_4\text{–O–}CrO_3H_2{}^+ \xrightarrow{\text{slow}} \underset{\mathbf{I_a}}{C_5H_8O_5\text{–}CrO^{2+}} + OH^- + H_2O \quad (5)$$

$$\underset{\mathbf{I_a}}{C_5H_8O_5\text{–}CrO^{2+}} + H^+ \rightleftarrows C_5H_8O_5\text{–}CrOH^{3+} \quad (6)$$

$$C_5H_8O_5\text{–}CrOH^{3+} \xrightarrow{\text{slow}} C_5H_6O_5\text{–}Cr^{2+} + H_3O^+ \quad (7)$$

$$C_5H_6O_5\text{–}Cr^{2+} + C_5H_8O_5\text{–}CrOH^{3+} \rightarrow \underset{\mathbf{I_b}}{C_5H_5O_5\text{–}Cr^{2+}} + Cr^{3+} + C_5H_8O_5 + H_2O \quad (8)$$

$$\underset{\mathbf{I_b}}{C_5H_5O_5\text{–}Cr^{2+}} + O_2 \xrightarrow{\text{slow}} Cr^{3+} + C_5H_4O_6 + OH^- \quad (9)$$

where $C_5H_{10}O_5$ is the empirical formula of D-ribose.

Usually, in the mechanism of a given reaction there is only one slow step for each reaction pathway considered; this happens when all the intermediates involved are short-lived (in steady state). In the mechanism proposed above, the existence of three slow steps explains the appearance of two long-lived intermediates.

In eqn. (4) and (6) the protonation of an oxygen atom belonging to the chromium moiety of the respective reactant molecules has been proposed. The result of this protonation is a decrease of the electron density on the chromium atom and, so, an enhancement of its oxidizing power. Thus, eqn. (5), (7) and (8), where the protonated chromium moiety acts as oxidant, are facilitated. From the plot given in Fig. 3, the equilibrium constant for the protonation of $\mathbf{I_a}$, eqn. (6), has been obtained: $K_6 = 4.5 \pm 1.1\ \mathrm{M}^{-1}$, at ionic strength 1.19 M and 30.0 °C.

It has long been discussed what is the actual fate of the intermediate Cr(IV) in the reactions of Cr(VI) with organic substrates. Half a century ago, Westheimer[28] proposed two mechanisms. In the first, Cr(IV) was oxidized by Cr(VI), but this is in disagreement with experimental results based on the study of the inhibition by Mn^{2+} [it competes for Cr(IV) with the organic substrate instead of with Cr(VI)].[29] In the second mechanism, Cr(IV) suffers a 2-electron reduction by the organic substrate. A third mechanism was proposed later, involving a 1-electron reduction of Cr(IV) by the organic substrate.[30] Recently, the detection of $CrOO^{2+}$ in O_2-containing aqueous solutions evidenced that, with a few exceptions such as cyclobutanol and pivaldehyde that behave as 1-electron reductants, most organic substrates behave as 2-electron reductants toward Cr(IV).[7]

In the present case, the formation of the intermediate $\mathbf{I_b}$ seems to imply that the organic substrate behaves toward Cr(IV) (intermediate $\mathbf{I_a}$) as both a 2-electron reductant [yielding Cr(II) in eqn. (7) by hydride-ion transfer] and as a 1-electron reductant [yielding Cr(III) in eqn. (8) by hydrogen-atom transfer]. The detection of a dimeric form of Cr(III) between the products of the Cr(VI)/D-ribose reaction[10] supports the involvement in the mechanism of Cr(II) as an intermediate.

It should be noticed that the last step [eqn. (9)] in the mechanism proposed above is not actually elementary. Instead, it represents the idealized stoichiometry of a chain reaction.[18] The finding that $Na_4P_2O_7$ was around 500 times more efficient as inhibitor than H_3PO_4 for the decomposition of $\mathbf{I_b}$ in the presence of Mn^{2+} suggests that Mn^{3+} (for which pyrophosphate is a stabilizing ligand[31]) might be an active intermediate in that decomposition. Mn^{3+} is actually formed from the 1-electron oxidation of Mn^{2+} by Cr(IV).[6]

This means that the kinetic order (1.66 ± 0.06) found for $\mathbf{I_b}$ in its decomposition in the presence of Mn^{2+} must be considered only as an apparent value, because in the series of experiments with increasing initial concentration of $\mathbf{I_b}$ done to determine its order the concentration of Cr(IV) (intermediate $\mathbf{I_a}$) increased too, given that at the instant when $\mathbf{I_b}$ reached its maximum concentration the intermediate $\mathbf{I_a}$ was also present.

Another pathway for the formation of Mn^{3+} might be the 1-electron oxidation of Mn^{2+} by free radicals. According to the mechanism proposed for the decomposition of CrR^{2+} in O_2-containing aqueous solutions the chain carriers are the free radicals $R^\bullet$ and $ROO^\bullet$, and the latter are known to be able to oxidize Mn^{2+}.[18]

Since neither D-mannitol, a scavenger for hydroxyl free radicals,[32] nor superoxide dismutase had any appreciable effect on the decomposition of $\mathbf{I_b}$ in the presence of Mn^{2+}, the participation of hydroxyl or superoxide radicals as active intermediates in that decomposition can be excluded.

Autocatalysis may be caused, in principle, either by a reaction product or by a long-lived intermediate capable of accumulating in a high enough concentration. On the contrary, unstable intermediates are not likely to act as autocatalytic agents, because during most of the kinetic run their concentrations are in continuous depletion. In the present case, given the relative chemical inertness of the reaction products (Cr^{3+} and an oxidized form of D-ribose), the slight autocatalysis found in the decomposition of $\mathbf{I_b}$ in the presence of Mn^{2+} was probably caused by a long-lived intermediate involved in that decomposition. Thus, since the free radicals of the types $R^\bullet$ and $ROO^\bullet$ involved in the chain reaction are rather unstable, a likely possibility for the autocatalyst might be Mn^{3+}, given that the experimental results seem to indicate its participation as an active intermediate in the decomposition of $\mathbf{I_b}$.

According to the results shown in Table 1, the yield of $\mathbf{I_b}$ at the instant of its maximum concentration was around 6% referred to the initial Cr(VI). The molar absorption coefficient obtained for $\mathbf{I_b}$ was $\varepsilon_{297} \simeq 7 \times 10^3\ \mathrm{M^{-1}\ cm^{-1}}$, in good agreement with the values reported for species of the type CrR^{2+}.[17] The low yield of $\mathbf{I_b}$ can be explained by considering the following. (i) Some intermediate $\mathbf{I_a}$ is reduced to Cr(II) while Cr(VI) is still present in the solution. This Cr(II) will be oxidized to Cr(III) without formation of $\mathbf{I_b}$. (ii) When $\mathbf{I_b}$ reaches its maximum concentration some $\mathbf{I_a}$ is still present in the solution, whereas some $\mathbf{I_b}$ has already been oxidized by O_2 to Cr(III). (iii) Other pathways not involving $\mathbf{I_b}$ as intermediate might also contribute to the global reaction. For instance, some of the Cr(II) formed from $\mathbf{I_a}$ might be oxidized directly by O_2 without formation of $\mathbf{I_b}$.

Biological relevance

The existence of two long-lived complexes of chromium in a low oxidation state with D-ribose (a key component of RNA) is certainly interesting in relation to the problem of the explanation of chromate toxicity and carcinogenesis, since it is believed that their expression requires the previous metabolization of Cr(VI) by appropriate intracellular reducing agents.[33] However, since the work on these intermediates was made in acidic media, and the reaction between Cr(VI) and D-ribose in neutral aqueous solutions is extremely slow, an extrapolation of these results to physiologically relevant conditions seems too far-fetched at the present moment. However, the formation of these intermediates under physiological conditions cannot be discarded, although at least the initial step in the reduction of Cr(VI) should be provoked by reductants (such as ascorbic acid[34] or glutathione[35]) stronger than D-ribose.

References

1 J. F. Perez-Benito, C. Arias, R. M. Rodriguez and M. Ros, *New J. Chem.*, 1998, **22**, 1445.
2 D. M. L. Goodgame, P. B. Hayman and D. E. Hathway, *Polyhedron*, 1982, **1**, 497.
3 C. Palopoli, S. Signorella and L. F. Sala, *New J. Chem.*, 1997, **21**, 343.
4 A. Sreedhara, N. Susa and C. P. Rao, *Inorg. Chim. Acta*, 1997, **263**, 189.
5 J. F. Perez-Benito and C. Arias, *New J. Chem.*, 1999, **23**, 945.
6 J. K. Beattie and G. P. Haight, in *Inorganic Reaction Mechanisms, Part II*, ed. J. O. Edwards, Wiley, New York, 1972, p. 100.
7 S. L. Scott, A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1992, **114**, 4205.
8 S. L. Scott, A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1991, **113**, 7787.
9 M. C. Ghosh and E. S. Gould, *Inorg. Chem.*, 1991, **30**, 491.
10 S. P. Kaiwar, M. S. S. Raghavan and C. P. Rao, *J. Chem. Soc., Dalton Trans.*, 1995, 1569.
11 J. H. Espenson, *Acc. Chem. Res.*, 1970, **3**, 347.
12 J. H. Espenson, A. Bakac and J. Janni, *J. Am. Chem. Soc.*, 1994, **116**, 3436.
13 A. Bakac, S. L. Scott, J. H. Espenson and K. R. Rodgers, *J. Am. Chem. Soc.*, 1995, **117**, 6483.
14 A. Bakac, *Prog. Inorg. Chem.*, 1995, **43**, 267.
15 A. Bakac and J. H. Espenson, *Acc. Chem. Res.*, 1993, **26**, 519.
16 M. E. Brynildson, A. Bakac and J. H. Espenson, *J. Am. Chem. Soc.*, 1987, **109**, 4579.
17 J. P. Leslie and J. H. Espenson, *J. Am. Chem. Soc.*, 1976, **98**, 4839.
18 D. A. Ryan and J. H. Espenson, *J. Am. Chem. Soc.*, 1982, **104**, 704.
19 J. H. Espenson, *Chemical Kinetics and Reaction Mechanisms*, McGraw-Hill, New York, 1995, p. 184.
20 R. M. Sellers and M. G. Simic, *J. Am. Chem. Soc.*, 1976, **98**, 6145.
21 J. K. Kochi and R. V. Subramanian, *J. Am. Chem. Soc.*, 1965, **87**, 4855.
22 J. K. Kochi, A. Bemis and C. L. Jenkins, *J. Am. Chem. Soc.*, 1968, **90**, 4616.
23 F. A. L. Anet and E. Leblanc, *J. Am. Chem. Soc.*, 1957, **79**, 2649.
24 D. Dodd and M. D. Johnson, *J. Chem. Soc. (A)*, 1968, 34.
25 R. G. Coombes, M. D. Johnson and D. Vamplew, *J. Chem. Soc. (A)*, 1968, 2297.
26 D. Dodd, M. D. Johnson and D. Vamplew, *J. Chem. Soc. (B)*, 1971, 1841.
27 R. S. Nohr and J. H. Espenson, *J. Am. Chem. Soc.*, 1975, **97**, 3392.
28 F. H. Westheimer, *Chem. Rev.*, 1949, **45**, 419.
29 J. F. Perez-Benito and C. Arias, *Can. J. Chem.*, 1993, **71**, 649.
30 J. Rocek and C. S. Ng, *J. Am. Chem. Soc.*, 1974, **96**, 1522, 2840.
31 L. I. Simandi and M. Jaky, *J. Am. Chem. Soc.*, 1976, **98**, 1995.
32 M. Itoh, M. Nakamura, T. Suzuki, K. Kawai, H. Horitsu and K. Takamizawa, *J. Biochem.*, 1995, **117**, 780.
33 S. L. Brauer, A. S. Hneihen, J. S. McBride and K. E. Wetterhahn, *Inorg. Chem.*, 1996, **35**, 373.
34 L. Zhang and P. A. Lay, *J. Am. Chem. Soc.*, 1996, **118**, 12624.
35 J. F. Perez-Benito, D. Lamrhari and C. Arias, *J. Phys. Chem.*, 1994, **98**, 12621.