Reactions of aquatitanium(II) with hypervalent chromium species

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Tables S1 to S5. Detailed kinetic data for redox reactions.

Fig S1. Kinetic Profile for the reaction of chromium(IV) with titanium(II) in solutions buffered by 2-ethyl-2-hydroxybutanoate(Lig⁻).

Fig S2. $k_{1(obs)}$/[Ti(II)] vs. [Ti(IV)] for $Cr^{VI} \longrightarrow Cr^{V}$ according to Table S4.

Table S1. Reduction of chromium(IV) by titanium(II) in solutions buffered by 2-ethyl-2-Hydroxybutanoate (Lig⁻). Kinetic data.[a]

[Ti(II)]/ mM	[Ti(IV)]/ mM	$10^{-2}k_{obs}$, s^{-1} [b]
0.25	0.25	1.43 (1.41)
0.50	0.50	2.8 (2.8)
0.60	0.60	3.4 (3.4)
0.75	0.75	4.1 (4.2)

[a]Reactions were run at $22.0 \pm 0.5\ ^{o}C$; $[HLig] + [Lig^-] = 0.28$ M, $[Cr(IV)] = 5.0 \times 10^{-5}$ M, $\mu = 0.50$ M $(NaClO_4 + Lig^-)$, pH = 3.08, $\lambda = 510$ nm.

[b]Pseudo-first order rate constants; parenthetical values were calculated using rate law: $k_{obs} = [Ti^{II}](5.5 \times 10^5\ M^{-1}s^{-1})$.

Table S2. Reduction of chromium(V) by titanium(II) in solutions buffered by 2-ethyl-2-

hydroxybutanoate (Lig⁻). Kinetic data.[a]

[Ti(II)]/mM	[Ti(IV)]/mM	k_{obs}, s^{-1} [b]
0.50	0.50	26(26)
0.70	0.70	36(36)
1.00	1.00	52(51)
1.50	1.50	75(77)
0.50	1.00	25(26)
0.50	1.50	26(26)

[a]Reactions at 22.0 ± 0.5 °C; $[Cr^V] = 5.0 \times 10^{-5}$ M; $[HLig] + [Lig^-] = 0.28$ M; $\mu = 0.50$ M

$(NaClO_4 + Lig^-)$; $\lambda = 510$ nm; pH $= 3.1$.

[b]Pseudo-first order rate constants; parenthetical values were calculated as $k_{obs} = [Ti^{II}]$

$(5.1 \times 10^4$ M^{-1}s$^{-1})$.

Table S3. Reduction of Cr(VI) by Ti(II) in the absence of ligands stabilizing Cr(V) and Cr(IV).Kinetic data[a]

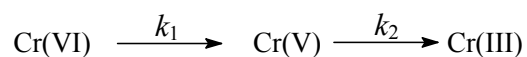| [Ti(II)], mM	[Ti(IV)], mM	[H$^+$], M	k_{obs}, s^{-1} [b]	k_{obs}, s^{-1} [c]
1.00	1.00	0.50	11.2(11.3)	9.0(9.8)
1.50	1.50	0.50	17.1(17.0)	14.6(14.8)
2.0	2.0	0.50	23(23)	19.6(19.7)
3.0	3.0	0.50	34(34)	32(29)
5.0	5.0	0.50	57(57)	51(49)
1.00	5.0	0.50	11.4(11.3)	9.6(9.8)
1.00	10.0	0.50	11.1(11.3)	9.2(9.8)
1.00	1.00	0.35	8.6(8.6)	8.2(8.1)
1.00	1.00	0.25	6.8(6.8)	7.2(6.9)
1.00	1.00	0.100	4.1(4.1)	5.1(5.2)
1.00	1.00	0.050	3.2(3.2)	4.6(4.6)

[a]Reactions at 22.0±0.5 °C, μ = 0.50 M, λ = 350 nm; [Cr^{VI}] = 5 × 10^{-5} M. All curves were exponential.

[b]Pseudo-first order rate constants in perchorate media.   Parenthetical values were calculated using rate law $k_{obs} = (k_o + k_H[H^+])[Ti^{II}]$, where k_o = (23 ± 1) × 10^2 M^{-1}s^{-1} and k_H = (18 ± 1) × 10^3 M^{-2}s^{-1}.

[c]Pseudo-first order rate constants in triflate media. Parenthethetical values were calculated usingrate law above, where $k_o = (41 \pm 1) \times 10^2$ M^{-1}s^{-1} and $k_H = (11.6 \pm 0.6) \times 10^3$ M^{-2}s^{-1}.

Table S4. Biphasic reaction of Cr(VI) and Ti(II) in ligating buffer (Lig$^-$) which stabilizes Cr(V)[a] Rise and fall profile showing generation and decay of Cr(V)-ligand complex.

$$Cr(VI) \xrightarrow{k_1} Cr(V) \xrightarrow{k_2} Cr(III)$$

[Ti^{II}]/ mM	[Ti^{IV}]/ mM	$(k_1)_{obs}$, s^{-1} [b]	$(k_2)_{obs}$; s^{-1} [c]
0.50	0.50	6.4 (6.4)	32 (29)
0.80	0.80	15.8 (15.8)	48 (47)
1.00	1.00	24 (23)	59 (58)
1.50	1.50	50 (49)	80 (87)
2.0	2.0	83 (83)	109 (116)
2.5	2.5	121 (122)	139 (145)
0.50	1.00	12.0 (11.9)	29 (29)
0.50	1.50	17.1 (16.8)	31 (29)
0.50	2.0	21 (21)	30 (29)
0.50	2.5	24 (24)	30 (29)
0.50	3.0	28 (28)	29 (29)
0.50	3.5	31 (30)	29 (29)
0.50	4.0	34 (33)	29 (29)
0.50	5.0	37 (37)	30 (29)
0.50	6.0	39 (41)	28 (29)

[a]Reactions were carried out at 22.0 $\pm$ 0.5 $^\circ$C; [HLig] + [Lig$^-$] = 0.285 M; μ = 0.50 M

(NaClO$_4$ + Lig$^-$); pH 3.08; λ = 510 nm; [Cr^{VI}] = 0.05 − 0.20 mM. Contributing rate

constants were calculated as described by Bose (ref. 18a).

[b]Parenthetical values were calculated using rate law (5) and parameters in text.

[c]Parenthetical values were calculated as k_2 = [Ti^{II}](5.9 × 10^4 M^{-1} s^{-1}).

Table S5. Reductions of Cr(VI) and Cr(IV) by Ti(III). Kinetic data.[a]

Oxidant	[Ti(III)]/ mM	k_{obs}, s^{-1}
Cr(VI)[b]	1.00	4.3 (4.1)[d]
	3.00	13.0 (12.3)[d]
	5.00	19.3 (20.0)[d]
	8.00	32 (33)[d]
Cr(IV)[c]	0.60	80 (78)[e]
	0.80	106 (104)[e]
	1.00	128 (130)
	1.20	150 (156)[e]

[a]Reactions at 22.0 ± 0.5 °C. All curves were exponential.

[b]μ = 0.50 M (HCl/HClO$_4$); λ = 350 nm, [Cr^{VI}] = 1.0 × 10^{-4} M; no 2-methyl-2-hydroxybutanoate(Lig$^-$) added.

[c]pH 3.50, [HLig] + [Lig$^-$] = 0.010 M; μ = 0.10 M (LiCl) λ = 510 nm; [Cr^{IV}] = 1.0 × 10^{-4} M.

[d]Pseudo-first order rate constants; parenthetical values were calculated using rate law: k_{obs} = [Ti^{III}](4.1 × 10^3 M^{-1}s^{-1}).

[e]Pseudo-first order rate constants; parenthetical values were calculated using rate law: k_{obs} = [Ti^{III}](1.3 × 10^4 M^{-1}s^{-1}).
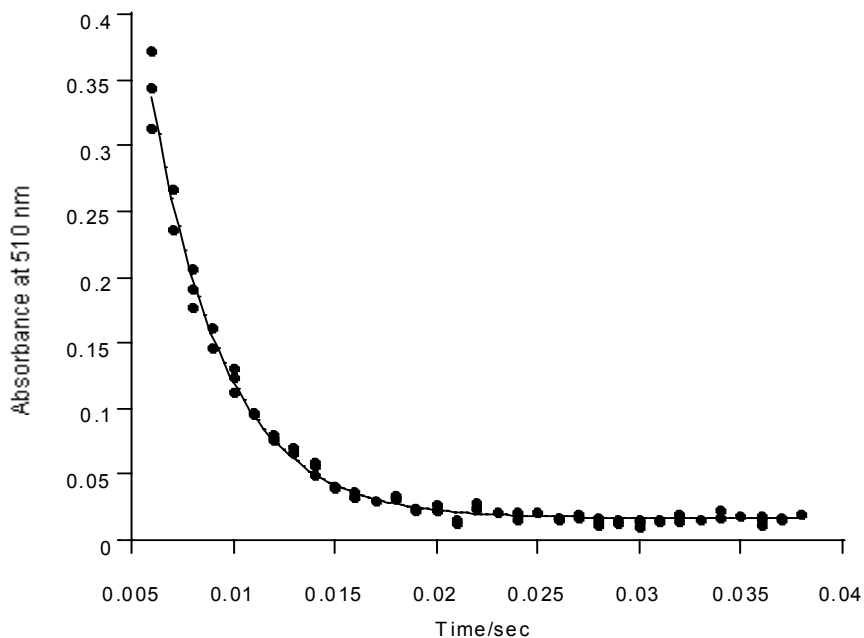
Fig. S1. Kinetic profile at 510 nm for the reaction of chromium(IV) (5.0×10^{-5} M) with

titanium(II) (5.0×10^{-4} M) in solutions buffered by 2-ethyl-2-hydroxybutanoate(Lig^-) at

22.0 ± 0.5 °C. The pH was 3.08. [HLig] + [Lig^-] = 0.28 M, μ = 0.50 M ($NaClO_4$ + Lig^-).

Small circles denote experimental data; the solid line was calculated using first order rate

law: $A_t = A \exp^{-kt} + A_\infty$ where A_t, A, A_∞ and k represent absorbance at time t, total

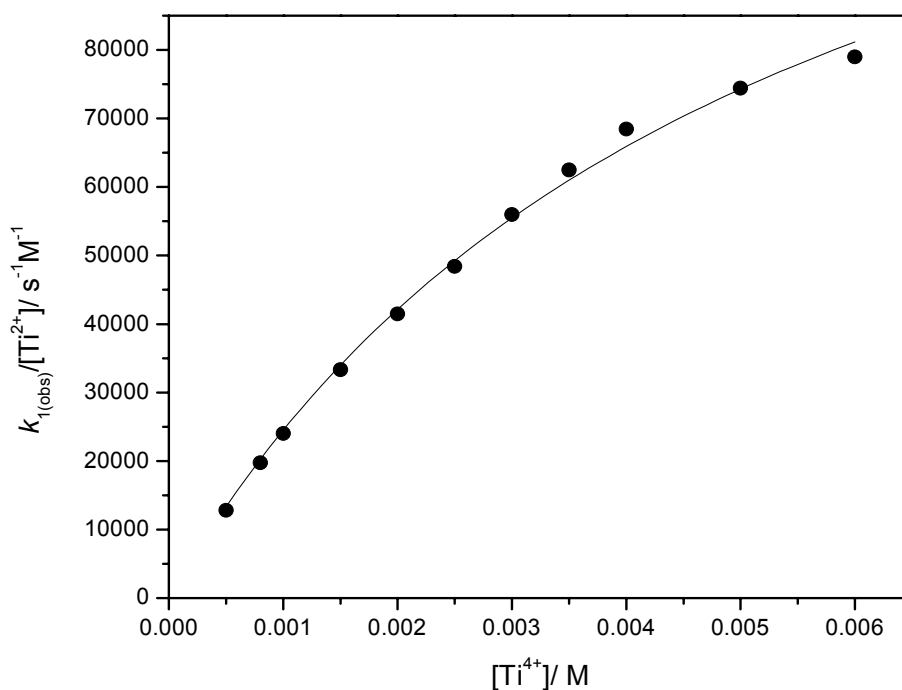absorbance change, final absorbance and rate constant respectively.

Fig. S2. $k_{1(obs)}/[Ti(II)]$ vs. [Ti(IV)] for $Cr^{VI} \longrightarrow Cr^{V}$ according to table S-4. [Ti(II)] = $(0.50 - 2.5)$ mM; [Ti(IV)] = $(0.50 - 6.0)$ mM. All the reactions were carried out at 22.0 ± 0.5 °C; [HLig] + [Lig⁻] = 0.285 M; μ = 0.50 M (NaClO$_4$ + Lig⁻); pH 3.08; λ = 510 nm; [Cr^{VI}] = $(0.05 - 0.20)$ mM. Solid line represents calculated values using the equation: $k_{1(obs)}/[Ti^{2+}] = k_{cat}K[Ti^{IV}]/(1+K[Ti^{IV}])$ taking k_{cat} = $(15.8 \pm 0.7) \times 10^4$ M^{-1}s^{-1} and $K = (1.8 \pm 0.1) \times 10^2$ M^{-1}.