Electronic Supplementary Information for Dalton Transactions

REDUCTIONS BY AQUATITANIUM(II)

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SUPPLEMENTARY MATERIALS

Tables S-1 to S-6. Detailed kinetic data for redox reactions.

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Table S-1. Reduction of $[(NH_3)_5Co(H_2O)]^{3+}$ by Ti(II); kinetic data[a]

[Ti(II)], mM	$[H^+]$, M	$10k_2$, M^{-1} s^{-1} [b]
7.3	0.50	0.70 (0.63)
11.0	0.50	0.72 (0.63)
16.0	0.50	0.77 (0.63)
25.0	0.50	0.70 (0.63)
6.6	0.20	1.64 (1.58)
6.6	0.25	1.29 (1.27)
6.6	0.30	1.05 (1.06)
6.6	0.35	0.85 (0.90)
6.6	0.40	0.77 (0.79)
6.6	0.45	0.70 (0.70)
6.6	0.50	0.65 (0.63)

[a]Reactions were carried out at 22 °C; μ = 0.50M ($HClO_4/NaClO_4$), $[Co^{III}]$ = 1.0-1.5 mM; λ = 491 nm. [b]Second order rate constants; parenthetical values were calculated using rate law (4) in text, taking $k = 3.2 \times 10^{-2}$ s^{-1}.

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Table S-2. Reduction of 2,5-dichloro-3,6-dihydroxybenzoquinone (CHBzqn) with titanium(II); kinetic data.[a]

[Ti(II)], mM	$[H^+]$, M	$10^{-2}k_2$, $M^{-1}s^{-1}$ [b]
0.17	0.50	6.2 (6.5)
0.33	0.50	6.2 (6.5)
0.50	0.50	5.7 (6.5)
0.66	0.50	5.8 (6.5)
0.17	0.050	10.8 (11.2)
0.17	0.10	9.0 (8.6)
0.17	0.20	7.6 (7.3)
0.17	0.30	6.9 (6.9)
0.17	0.40	6.5 (6.7)

[a]Reactions were carried out at 22 ^oC; μ = 0.50 ($HClO_4/NaClO_4$); [CHBzqn] = 0.025 mM throughout; λ = 302 nm. [b]Second order constants; parenthetical values were calculated using rate law (7) and parameters in Table 2.

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Table S-3. Reduction of 2,5-dichloro-3,6-dihydroxybenzoquinone (CHBzqn) with titanium(III); kinetic data.[a]

[Ti(III)], mM	$[H^+]$, M	$10^{-4}k_2$, M^{-1} s^{-1} [b]
0.056	0.50	0.69 (0.66)
0.110	0.50	0.59 (0.66)
0.23	0.50	0.61 (0.66)
0.50	0.50	0.63 (0.66)
0.056	0.050	5.8 (6.6)
0.056	0.10	3.7 (3.3)
0.056	0.15	2.6 (2.2)
0.056	0.20	1.73 (1.66)
0.056	0.30	1.14 (1.10)
0.056	0.40	0.80 (0.83)
0.056	0.45	0.71 (0.74)
0.056	0.50	0.63 (0.66)

[a]Reactions were carried out at 22 ^oC; μ = 0.50 M ($HClO_4/NaClO_4$), [CHBzqn] = 0.010-0.012 mM; λ = 302 nm. [b]Second order rate constants; parenthetical values were calculated using rate law and parameter in Table 3.

Table S-4 Reduction of benzoquinone (Bzqn) with titanium(III); kinetic data.[a]

[Ti(III)], mM	$[H^+]$, M	$10^{-4}k_2$, M^{-1} s^{-1} [b]
0.15	0.50	1.43 (1.51)
0.30	0.50	1.43 (1.51)
0.45	0.50	1.38 (1.51)
0.60	0.50	1.33 (1.51)
0.30	0.050	5.7 (5.9)
0.30	0.10	3.5 (3.5)
0.30	0.15	2.7 (2.6)
0.30	0.20	2.3 (2.2)
0.30	0.30	2.00 (1.70)
0.30	0.40	1.60 (1.64)

[a]Reactions were carried out at 22 °C; μ = 0.50 M ($HClO_4$/$NaClO_4$); [Bzqn] = 0.020 mM throughout; λ = 502 nm. [b]Second order rate constants; parenthetical values were calculated using rate laws and parameters in Table 3.

Table S-5. Reduction of tri-iodide with titanium(II); kinetic data[a]

[Ti(II)], mM	[I^-], M	[H^+], M	k, M^{-1} s^{-1} [b]
1.66	0.050	0.050	0.30 (0.27)
3.33	0.050	0.050	0.32 (0.27)
6.66	0.050	0.050	0.33 (0.27)
13.3	0.050	0.050	0.31 (0.27)
3.0	0.050	0.10	1.30 (1.34)
3.0	0.050	0.11	1.10 (1.22)
3.0	0.050	0.15	0.85 (0.80)
3.0	0.050	0.20	0.65 (0.67)
3.0	0.050	0.30	0.45 (0.45)
3.0	0.050	0.40	0.39 (0.34)
3.0	0.0010	0.50	4.0 (3.6)
3.0	0.0020	0.50	2.2 (2.6)
3.0	0.0050	0.50	1.60 (1.42)
3.0	0.010	0.50	0.82 (0.84)
3.0	0.020	0.50	0.49 (0.50)
3.0	0.050	0.50	0.30 (0.27)
3.0	0.080	0.50	0.20 (0.21)
3.0	0.100	0.50	0.174 (0.187)

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[a]Reactions were carried out at 22 ^{o}C; μ = 0.50 M (HCl/LiCl/CF_3SO_3H); $[I_3^-]$ = 0.010 mM throughout; λ = 352 nm. [b]Second order rate constants; parenthetical values were calculated using rate law (8) in text and parameters in Table 2.

Table S-6. Reduction of tri-iodide with titanium(III); kinetic data[a]

[Ti(III)], mM	[I^-], M	[H^+], M	k, $M^{-1}s^{-1}$ [b]
9.3	0.050	0.50	0.34 (0.33)
18.6	0.050	0.50	0.36 (0.33)
28.0	0.050	0.50	0.33 (0.33)
37.3	0.050	0.50	0.33 (0.33)
20.0	0.0010	0.50	2.6 (2.6)
20.0	0.0050	0.50	1.07 (1.10)
20.0	0.010	0.50	0.69 (0.71)
20.0	0.015	0.50	0.56 (0.56)
20.0	0.020	0.50	0.51 (0.48)
20.0	0.030	0.50	0.42 (0.40)
20.0	0.040	0.50	0.38 (0.33)
8.5	0.050	0.10	16.0 (16.3)
8.5	0.050	0.15	1.06 (1.08)
8.5	0.050	0.20	0.78 (0.81)
8.5	0.050	0.25	0.64 (0.65)
8.5	0.050	0.30	0.55 (0.54)
8.5	0.050	0.40	0.30 (0.41)
8.5	0.050	0.50	0.33 (0.33)

[a]Reactions were carried out at 22 ^oC; μ = 0.50 M ($HCl/LiCl/CF_3SO_3H$); [I_3^-] = 0.020 mM throughout, λ = 352 nm. [b]Second order rate constants; parenthetical values were calculated using rate law (8) in text and parameters in Table 3.