Electronic Supplementary Information for Dalton Transactions

Reductions of oxo species by aquatitanium(II) as catalyzed by titanium(IV)

Basab Bijayi Dhar and Edwin S. Gould

SUPPLEMENTARY MATERIALS

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

Fig. 1. Reduction of 1,4-benzoquinone by Ti(II) as catalyzed by Ti(IV); kinetic dependence on [Ti(IV)].

Fig. 2. Absorbance of Ti(II)-Ti(IV) mixtures.

Table S1 – Titanium(II) reduction of 1,4-benzoquinone as catalyzed by titanium(IV); kinetic data[a]

$10^4[Ti^{II}]$/ M	$10^3[Ti^{IV}]$/ M	$[H^+]$/ M	$10^3 k_{obs}$/ s^{-1} [b]
1.00	1.00	0.50	3.0 (3.1)
2.0	1.00	0.50	6.2 (6.17)
4.0	1.00	0.50	13.1 (12.3)
6.0	1.00	0.50	18.2(18.5)
8.0	1.00	0.50	24(25)
10.0	1.00	0.50	31(31)
10.0	1.00	0.50	37(37)
10.0	1.60	0.50	42(42)
10.0	2.0	0.50	48(48)
10.0	4.0	0.50	63(64)
10.0	8.0	0.50	78(83)
10.0	10.0	0.25	31(31)
10.0	10.0	0.100	29(31)

[a]Reactions at 22.0 ± 0.5 °C, μ = 0.50 M ($HClO_4/NaClO_4/CF_3SO_3H$) λ = 246-260 nm; [Bzqn] = 1.0×10^{-5} M. [b]Pseudo-first order rate constants; parenthetical values were calculated using rate law and parameters in Table 2.

Table S2 – Titanium(II) reduction of 2,5-dichloro-3,6-dihydroxy-benzoquinone as catalyzed by titanium(IV); kinetic data[a]

$[Ti^{II}]$/ mM	$[Ti^{IV}]$/ mM	$[H^+]$/ M	$10k_{obs}$/ s^{-1} [b]
1.00	1.00	0.50	2.6(2.6)
1.00	3.0	0.50	5.0(5.0)
1.00	5.0	0.50	6.1(6.2)
1.00	8.0	0.50	7.1(7.2)
1.00	10.0	0.50	7.6(7.5)
2.0	8.0	0.50	15.6(14.3)
4.0	8.0	0.50	30(29)
6.0	8.0	0.50	42(43)
8.0	8.0	0.50	53(57)
2.0	2.0	0.50	8.2(8.2)
2.0	2.0	0.25	8.8(8.7)
2.0	2.0	0.100	10.7(10.9)

[a]Reactions at 22.0 ± 0.5 ^oC; μ = 0.50 M ($HClO_4/NaClO_4/CF_3SO_3H$) λ = 330 nm; [oxidant] = 5.0×10^{-5} M. [b]Pseudo-first order rate constants; parenthetical values were calculated using rate law and parameters in Table 2.

Table S3 – Titanium(II) reduction of 2,5-dihydroxy-1,4-benzoquinone, as catalyzed by titanium(IV); kinetic data[a]

$[Ti^{II}]$/ mM	$[Ti^{IV}]$/ mM	$[H^+]$/ M	$10k_{obs}$/ s^{-1} [b]
1.00	5.0	0.50	3.6(3.6)
2.0	5.0	0.50	7.3(7.2)
4.0	5.0	0.50	14.3(14.5)
5.0	5.0	0.50	18.3(18.1)
2.0	2.0	0.50	4.6(4.6)
2.0	3.0	0.50	5.8(5.8)
2.0	7.0	0.50	8.2(8.1)
2.0	10.0	0.50	9.0(9.0)
2.0	2.0	0.25	6.0(5.6)
2.0	2.0	0.100	8.3(8.4)

[a]Reactions at 22.0 ± 0.5 °C, μ = 0.50 M ($HClO_4$/$NaClO_4$/CF_3SO_3H), λ = 310 nm, [oxidant] = 1.0×10^{-5} M. [b]Pseudo-first order rate constants; parenthetical values were calculated using rate law and parameters in Table 2.

Table S4 – Titanium(II) reduction of tetrahydroxy-1,4-benzoquinone, as catalyzed by titanium(IV); kinetic data[a]

$[Ti^{II}]$/ mM	$[Ti^{II}]$/ mM	$[H^+]$/ M	$10k_{obs}$/ s^{-1} [b]
1.00	5.0	0.50	4.7(4.6)
2.0	5.0	0.50	8.5(9.1)
4.0	5.0	0.50	18.6(18.3)
5.0	5.0	0.50	22(23)
4.0	4.0	0.50	17.2(16.4)
4.0	6.0	0.50	20(20)
4.0	8.0	0.50	22(22)
4.0	10.0	0.50	24(24)
2.0	2.0	0.50	4.2(4.6)
2.0	2.0	0.25	4.0(4.6)
2.0	2.0	0.100	4.2(4.6)

[a]Reactions at 22.0 ± 0.5 °C, μ = 0.50 M ($HClO_4$/$NaClO_4$/CF_3SO_3H), λ = 310 nm, [oxidant] = 1.0×10^{-5} M. [b]Pseudo-first order rate constants; parenthetical values were calculated using rate law and parameters in Table 2.

Table S5 – Titanium(II) reduction of nitrosodisulfonate as catalyzed by titanium(IV); kinetic data[a]

$10^2[Ti^{II}]$/ M	$10^2[Ti^{IV}]$/ M	$[H^+]$/ M	k_{obs}/ s^{-1} [b]
1.00	1.00	0.50	32(30)
1.00	1.50	0.50	46(45)
1.00	2.0	0.50	60(59)
1.00	2.5	0.50	71(74)
1.50	2.5	0.50	95(112)
1.00	1.00	0.30	30(30)
1.00	1.00	0.100	30(30)

[a]Reactions at 22.0 ± 0.5 ^oC, μ = 0.50 M ($LiCl/CF_3SO_3H/HCl$), λ = 300 nm; [NDS] = 2.0 × 10^{-3} M. [b]Pseudo-first order rate constants; parenthetical values were calculated using the rate law and parameters in Table 2.

Table S6 – Titanium(II) reduction of manganese(IV) as catalyzed by titanium(IV); kinetic data[a]

$[Ti^{II}]$/ mM	$[Ti^{IV}]$/ mM	$[F^-]$/ mM	$[Cl^-]$/ mM	$[H^+]$/ M	k_{obs}/ s^{-1} [b]
1.00	1.00	0	0	0.50	2.4(2.8)
2.0	2.0	0	0	0.50	8.6(8.9)
3.5	3.5	0	0	0.50	22(21)
5.0	5.0	0	0	0.50	38(35)
7.0	7.0	0	0	0.50	55(54)
10.0	10.0	0	0	0.50	90(84)
1.00	2.0	0	0	0.50	4.3(4.5)
1.00	5.0	0	0	0.50	7.2(6.9)
1.00	8.0	0	0	0.50	8.6(8.0)
1.00	1.00	0	0	0.50	9.2(8.5)
1.00	1.00	1.00	0	0.50	3.9(4.1)
1.00	1.00	2.0	0	0.50	5.6(5.4)
1.00	1.00	5.0	0	0.50	9.2(9.3)
1.00	1.00	7.0	0	0.50	12.2(13.1)
1.00	1.00	10.0	0	0.50	17.2(16.0)
1.00	1.00	0	1.00	0.50	2.9(3.0)
1.00	1.00	0	5.0	0.50	4.0(4.0)
1.00	1.00	0	10.0	0.50	5.5(5.5)
1.00	1.00	0	0	0.10	2.5(2.8)

[a]Reductions of the biguanide complex, $[Mn^{IV}(bigH)_3]^{4+}$. Reactions were run at 22.0 ± 0.5 °C, μ = 0.50 M, ($HClO_4$/$NaClO_4$/CF_3SO_3H), λ = 430 nm. $[Mn^{IV}] = 1.0 \times 10^{-4}$ M. [b]Pseudo-first order rate constants; parenthetical values were calculated using rate laws and parameters in Table 2.

Figure captions:

Fig. 1 Plot of k_{obs} vs. [Ti(IV)] for the reduction of 1,4-benzoquinone by Ti(II). In all the sets, [Ti(II)] = 1.0 mM, [oxidant] = 0.010 mM, $[H^+]$ = 0.50 M, μ = 0.5 M ($HClO_4/CF_3SO_3H$) and T = 22.0 ± 0.5 °C. Solid line was calculated using rate law and kinetic parameters in Table 2.

Fig. 2 Absorbance at 428 nm vs. [Ti(IV)] for the Ti(II) solutions. In all the sets, [Ti(II)] = 1.0 mM, $[H^+]$ = 0.50 M, μ = 0.5 M ($HClO_4/CF_3SO_3H$), T = 22.0 ± 0.5 °C. Optical path length = 1.0 cm. Solid line represents calculated values using the equation:

$$\frac{Abs}{[Ti^{II}]} = \frac{\varepsilon_{Ti}^{II} + K\varepsilon_{Ti}^{II,IV}[Ti^{IV}]}{1 + K[Ti^{IV}]}$$

taking $\varepsilon_{Ti}^{II} = 0.33\ M^{-1}cm^{-1}$, $\varepsilon_{Ti}^{II,IV} = 19.3\ M^{-1}cm^{-1}$ and $K = 293\ M^{-1}$.

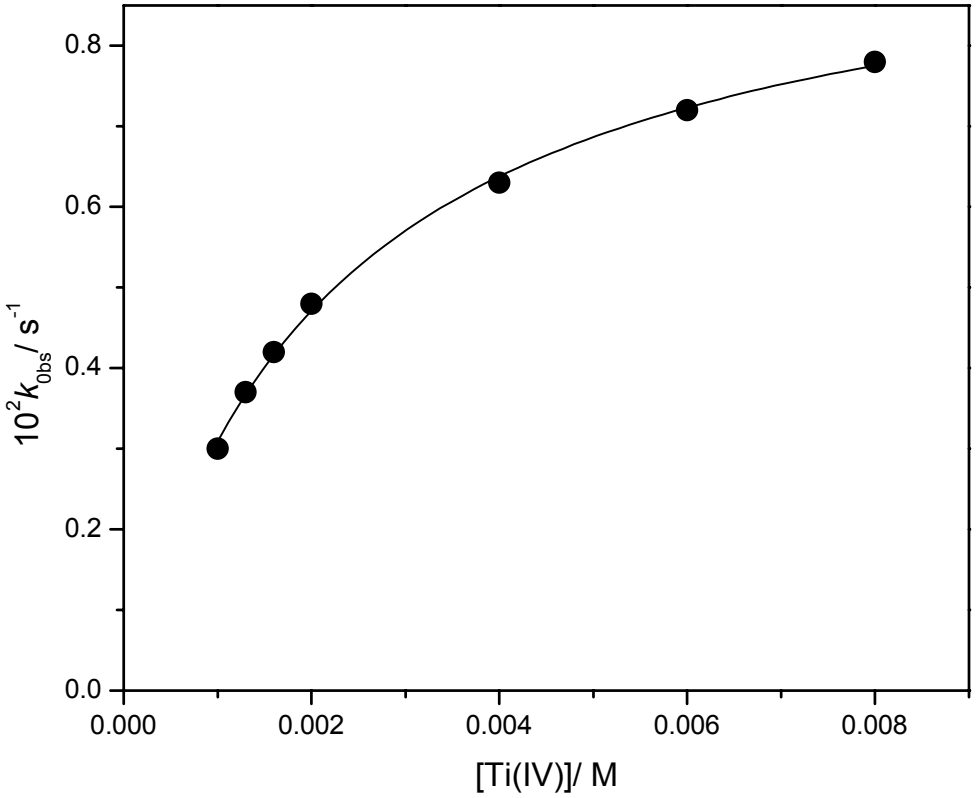

Fig. 1

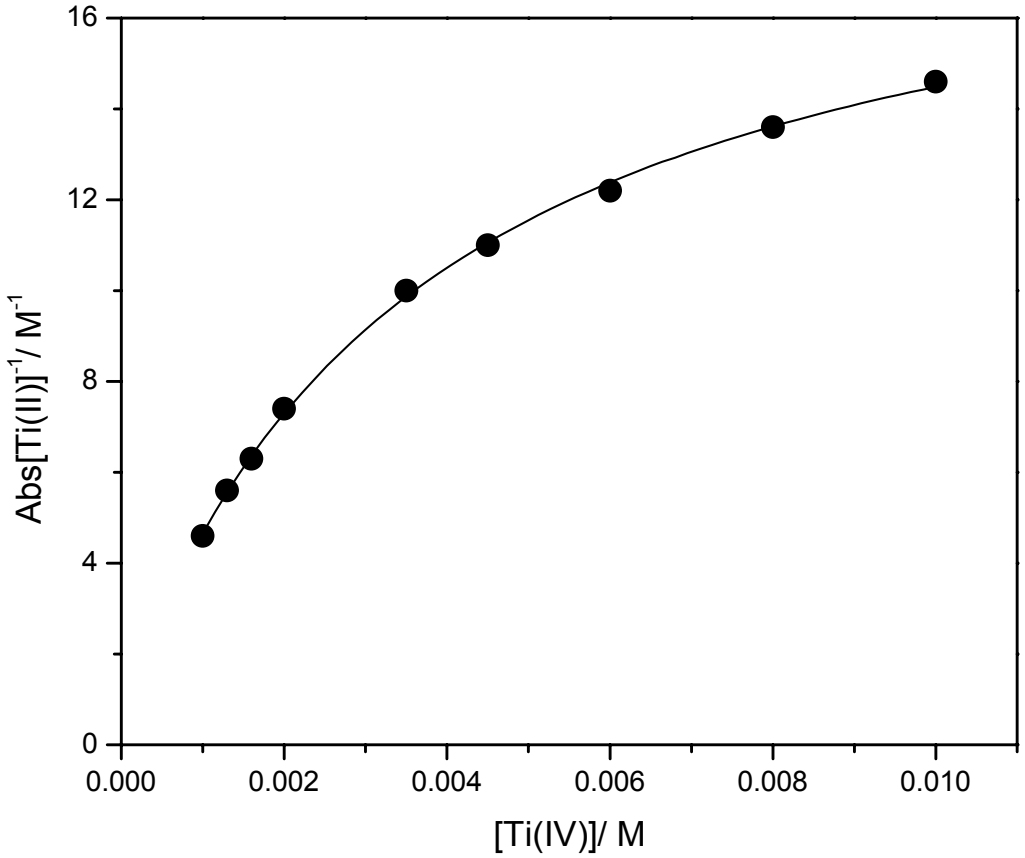

Fig. 2