

SUPPLEMENTARY MATERIALS

Tables S-1 to S-7. Detailed kinetic data for catalyzed redox reactions.

S-1

Table S-1. Reduction of vanadium(IV) by Ti(III), as catalyzed by molybdenum(VI),
kinetic data^a

[VO ²⁺], mM	[Mo ^{VI}], mM	[H ⁺], M	k_2 (M ⁻¹ s ⁻¹) ^b
12.0	0.50	0.50	13.5 (13.3)
16.0	0.50	0.50	13.4 (13.3)
20.0	0.50	0.50	13.3 (13.3)
26.0	0.50	0.50	13.5 (13.3)
20.0	0.50	0.10	13.6 (13.3)
20.0	0.025	0.50	2.4 (2.3)
20.0	0.050	0.50	2.8 (2.9)
20.0	0.10	0.50	4.0 (4.0)
20.0	0.20	0.50	6.3 (6.4)
20.0	0.25	0.50	7.0 (7.5)
20.0	1.0	0.50	25 (25)
20.0	2.5	0.50	65 (60)

^aReactions at 22 °C, μ = 0.50 M (HCl), [Ti^{III}] = 3.0 mM throughout; λ = 760 nm.

^bSecond order rate constants; parenthetical values were calculated using rate law (4) in text,

taking rate constants in Table 2.

Table S-2. Reduction of vanadium(IV) by titanium(II), as catalyzed by molybdenum(VI);

kinetic data^a

[VO ²⁺], mM	[Mo ^{VI}], mM	[H ⁺], M	k_2 (M ⁻¹ s ⁻¹) ^b
19.0	0.50	0.15	7.7 (7.8)
19.0	0.50	0.50	7.9 (7.8)
18.0	0.010	0.50	3.2 (3.3)
18.0	0.050	0.50	3.7 (3.7)
18.0	0.10	0.50	4.6 (4.2)
18.0	0.15	0.50	4.7 (4.6)
18.0	0.20	0.50	5.1 (5.1)
18.0	0.30	0.50	5.8 (6.0)
18.0	0.40	0.50	6.7 (6.9)
18.0	0.50	0.50	7.7 (7.8)
18.0	1.00	0.50	12.6
(12.3)			
10.0	0.50	0.50	7.9 (7.8)
14.0	0.50	0.50	7.6 (7.8)
28.0	0.50	0.50	7.7 (7.8)

^aReactions at 22 °C, μ = 0.50 M (CF₃SO₃H/HClO₄/NaClO₄); [Ti(II)] = 2.5 mM throughout;

λ = 760 nm.

^bSecond order rate constants; parenthetical values were calculated using rate law (4) in text,

taking rate constants in Table 2.

Table S-3. Reduction of vanadium(IV) by titanium(II), as catalyzed by copper(II);
kinetic data^a

[VO ²⁺], mM	[Cu ²⁺], mM	[H ⁺], M	k ₂ (M ⁻¹ s ⁻¹) ^b
19.0	0.50	0.10	7.9 (7.8)
19.0	0.50	0.25	7.9 (7.8)
19.0	0.50	0.50	8.0 (7.8)
18.0	0.010	0.50	3.3 (3.3)
18.0	0.050	0.50	3.7 (3.6)
18.0	0.10	0.50	4.0 (4.1)
18.0	0.15	0.50	4.5 (4.5)
18.0	0.20	0.50	4.8 (5.0)
18.0	0.30	0.50	5.7 (5.9)
18.0	0.40	0.50	6.9 (6.8)
18.0	1.00	0.50	12.6 (12.4)
11.0	0.50	0.50	7.8 (7.8)
22.0	0.50	0.50	8.0 (7.8)
33.0	0.50	0.50	7.9 (7.8)

^aReactions at 22.0 ± 0.5 °C, μ = 0.50 M (CF₃SO₃H/NaClO₄); [Ti^{II}] = 2.5 mM

throughout;

λ = 760 nm.

^bSecond order rate constants; parenthetical values were calculated using rate law (4)

in text,

taking rate constants in Table 2.

Table S-4. Reduction of benzoquinone by titanium(III), as catalyzed by molybdenum(VI),

kinetic data^a

[Ti(III)], mM	[Mo(VI)], mM	[H ⁺], M	10 ⁻² k ₂ , M ⁻¹ s ⁻¹ ^b
0.16	0	0.50	1.11 (1.13)
0.16	0.0030	0.50	1.80 (1.80)
0.16	0.0060	0.50	2.4 (2.5)
0.16	0.010	0.50	3.3 (3.4)
0.16	0.020	0.50	5.3 (5.6)
0.16	0.010	0.060	17.6 (19.9)
0.16	0.010	0.10	12.8 (12.3)
0.16	0.010	0.20	7.3 (6.7)
0.16	0.010	0.30	5.5 (4.9)
0.16	0.010	0.40	4.2 (3.9)
0.16	0.010	0.50	3.6 (3.4)
0.16	0.010	0.50	3.3 (3.4)
0.50	0.010	0.50	3.3 (3.4) ^c
0.66	0.010	0.50	3.2 (3.4) ^d

^aReactions at 22.0 ± 0.5 °C, $\mu = 0.50$ M (HCl), [Bzqn] = 0.020 mM throughout, [Cl⁻]

=

0.50 M unless otherwise indicated; $\lambda = 247$ nm. ^b Second order rate constants; parenthetical

values were calculated using rate law (5) in text, taking rate constants in Table 2.

^c[Cl⁻] = 0.10 M. ^d[Cl⁻] = 0.40 M.

S-5

Table S-5. Reduction of benzoquinone by titanium(II), as catalyzed by molybdenum(VI);

kinetic data^a

[Ti(III)], mM	[Me(VI)], mM	$10^{-2}k_2, \text{M}^{-1}\text{s}^{-1}$ ^b
0.10	0.010	6.6 (6.7)
0.16	0.010	6.6 (6.7)
0.20	0.010	6.6 (6.7)
0.30	0.010	6.6 (6.7)
0.10	0	2.0 (2.2)
0.10	0.0010	2.8 (2.6)
0.10	0.0020	3.4 (3.1)
0.10	0.0040	3.9 (4.0)
0.10	0.0060	5.1 (4.9)
0.10	0.0080	5.8 (5.8)
0.10	0.012	7.5 (7.5)
0.10	0.016	9.4 (9.3)

^aReactions at 22.0 ± 0.5 °C, $\mu = 0.50$ M (CF₃SO₃H), $\lambda = 247$ nm, [Bzqn] = 0.020 mM throughout, reactions independent of [H⁺] in the range 0.10-0.50 M.

^bSecond order rate constants; parenthetical values were calculated using rate law (4) in text

in conjunction with $k_o = 2.2 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$ and $k_{\text{cat}} = 4.5 \times 10^7 \text{ M}^{-2}\text{s}^{-1}$.

S-6

Table S-6. Reduction of I₃⁻ by titanium(III), as catalyzed by molybdenum(VI); kinetic data^a

[Ti(III)], mM	[Mo(VI)], mM	$k_2, \text{M}^{-1}\text{s}^{-1}{}^b$
8.5	0	0.33 (0.33)
5.0	0.0010	1.93 (1.83)
5.0	0.0020	3.3 (3.3)
5.0	0.0030	4.2 (4.8)
5.0	0.0040	6.4 (6.3)
5.0	0.0050	7.7 (7.8)
5.0	0.0080	13.4 (12.3)
5.0	0.012	19.1 (18.3)
5.0	0.020	31 (30)
5.0	0.040	62 (60)
1.5	0.10	160 (150)
3.0	0.10	155 (150)
4.5	0.10	154 (150)

5.0	0.10	149 (150)
6.0	0.10	147 (150)
5.0	0.20	296 (300)

^aReactions at 22.0 ± 0.5 °C, $\mu = 0.55$ M (0.50 M HCl/0.050 M KI), $[I_3^-]$ 0.25 mM throughout,

$\lambda = 450$ nm. Reactions independent of $[H^+]$ and $[Cl^-]$. ^bSecond order rate constants; Parenthetical values were calculated using rate law (4) in text in conjunction with the values

$k_o = 0.33$ M⁻¹s⁻¹ and $k_{cat} = 1.50 \times 10^6$ M⁻²s⁻¹.

S-7

Table S-7. Reduction of I_3^- by titanium(II), as catalyzed by molybdenum(VI); kinetic data^a

[Ti(II)], mM	[Mo(VI)], mM	k_2 , M ⁻¹ s ⁻¹ ^b
3.3	0	0.32 (0.32)
5.0	0.0010	1.04 (1.02)
5.0	0.0020	1.78 (1.73)
5.0	0.0040	2.8 (3.1)
5.0	0.0080	5.4 (5.9)
1.5	0.014	10.3 (10.2)
3.0	0.014	10.5 (10.2)
6.0	0.014	9.7 (10.2)
5.0	0.016	12.1 (11.6)
5.0	0.032	17.2 (22.9)
5.0	0.064	51 (45)
5.0	0.10	70 (71)
5.0	0.20	131 (141)

^aReactions at 22.0 ± 0.5 °C. $\mu = 0.55$ M (0.50 M CF₃SO₃H/0.050 M KI), [I₃⁻] = 0.25 mM;

$\lambda = 450$ nm. Reactions independent of [H⁺] and [Cl⁻]. ^bSecond order rate constants; parenthetical values were calculated using rate law (4) in text, taking $k_o = 0.32$ M⁻¹s⁻¹ and $k_{\text{cat}} = 7.1 \times 10^5$ M⁻²s⁻¹.