Electronic Supplementary Information for Dalton Transactions

Reactions of molybdenum (VI) with metal ion reductants

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SUPPLEMENTARY MATERIALS

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

Table S-1. The Mo(VI)-Ti(II) reaction; generation of Mo(V) transient. Kinetic data[a]

$[Ti^{II}]$, mM	$[H^+]$, M	10^{-3} k_{obsd}, $M^{-1}s^{-1}$ [b]
1.00	0.50	2.1 (2.0)
2.0	0.50	2.1 (2.0)
3.0[c]	0.50	2.2 (2.0)
5.0[c]	0.50	1.90 (2.0)
2.6	0.15	3.7 (3.8)
2.6	0.20	3.4 (3.3)
2.6	0.25	3.0 (3.0)
2.6	0.30	2.7 (2.7)
2.6	0.35	2.4 (2.5)
2.6	0.40	2.4 (2.3)
2.6	0.45	2.2 (2.1)
2.6	0.50	1.90 (2.0)
2.6	0.50	1.90[d] (2.0)
2.6	0.50	2.0[e] (2.0)

[a]Reactions at 22 ^oC, μ = 0.50 M (CF_3SO_3H/CF_3SO_3Na); λ = 430 nm $[Mo^{VI}]$ = 0.25 mM unless otherwise specified. [b]Second order rate constants; parenthetical values were calculated from eq. (8) in text, using parameters in Table 2. [c]$[Mo^{VI}]$ = 1.00 mM. [d]$[Cl^-]$ = 0.050 M. [e]$[Cl^-]$ = 0.30 M.

Table S-2 – The Mo(VI)-Ti(III) reaction; generation of the Mo(V) transient. Kinetic data[a]

[Ti(III)], mM	$[H^+]$, M	$[Cl^-]$, M	k_{obsd}, s^{-1} [b]
2.5	0.50	0.50	3.2 (3.4)
3.0	0.50	0.50	3.9 (3.8)
3.8	0.50	0.50	4.5 (4.6)
5.0	0.50	0.50	5.2 (5.3)
6.3	0.50	0.50	5.9 (6.0)
7.3	0.50	0.50	6.4 (6.5)
3.0	0.10	0.50	14.4 (15.3)
3.0	0.15	0.50	12.1 (11.1)
3.0	0.20	0.50	9.7 (8.7)
3.0	0.25	0.50	7.8 (7.2)
3.0	0.30	0.50	5.1 (6.1)
3.0	0.40	0.50	4.4 (4.7)
3.0	0.45	0.50	4.0 (4.2)
3.0	0.50	0.15	5.1 (4.6)
3.0	0.50	0.20	5.0 (4.5)
3.0	0.50	0.25	4.3 (4.4)
3.0	0.50	0.40	3.8 (4.0)
3.0	0.50	0.45	3.8 (3.9)
3.0	0.50	0.50	3.9 (3.8)

[a]Reactions at 22 °C, μ = 0.50 M (HCl/LiCl); [Mo(VI)] = 0.30 mM throughout.

[b]First order rate constants; parenthetical values were calculated using eq. (9) in text and parameters in Table 2.

Table S-3. The Mo(VI)-V(II) reaction; decay of the Mo(V) transient. Kinetic data[a]

[V(II)], mM	$[H^+]$, M	k_{obs}, s^{-1} [b]
6.0	0.50	1.05 (1.32)
10.0	0.50	1.03 (1.32)
20.0	0.50	1.06 (1.32)
12.0	0.15	2.7 (2.9)
12.0	0.20	2.5 (2.5)
12.0	0.25	2.3 (2.2)
12.0	0.30	2.0 (1.9)
12.0	0.40	1.55 (1.56)
12.0	0.45	1.37 (1.43)
12.0	0.50	1.18 (1.32)

[a]Reactions at 22 °C, μ = 0.50 M (CF_3SO_3H/CF_3SO_3Na); λ = 420 nm. $[Mo^{VI}]$ = 0.30 mM.

[b]First order rate constants; parenthetical values were calculated from eq. (10) in text, using parameters in Table 3.

Table S-4 – The Mo(VI)-Ti(II) reaction; decay of the Mo(V) transient. Kinetic data[a]

[Ti(II)], mM	[H^+], M	k_{obs}, s^{-1} [b]
2.0	0.50	1.04 (0.97)
2.6	0.50	1.05 (0.97)
3.0	0.50	1.11 (0.97)[c]
2.6	0.15	1.56 (1.57)
2.6	0.20	1.44 (1.45)
2.6	0.25	1.36 (1.34)
2.6	0.30	1.26 (1.24)
2.6	0.35	1.16 (1.16)
2.6	0.40	1.07 (1.09)
2.6	0.45	1.04 (1.03)
2.6	0.50	0.96 (0.97)
2.6	0.50	1.05 (0.97)[d]
2.6	0.50	0.97 (0.97)[d]

[a]Reactions at 22 °C, μ = 0.50 M (CF_3SO_3H/CF_3Na); λ = 420 nm [Mo^{VI}] = 0.25 mM unless otherwise indicated. [b]First order rate constants; parenthetical values were calculated from eq. (10) in text, using parameters in Table 3. [c][Mo(VI)] = 1.0 mM. [d][Cl^-] = 0.050 M. [e][Cl^-] = 0.40 M.

Table S-5. The Mo(VI)-Eu(II) reaction; decay of the Mo(V) transient. Kinetic data[a]

[Eu(II)], mM	$[H^+]$, M	$10^2[Cl^-]$, M	k_{obsed}, s^{-1} [b]
4.0	0.50	50	12.0 (14.5)
8.0	0.50	50	13.9 (14.5)
12.0	0.50	50	13.7 (14.5)
6.0	0.13	55	30 (30)
6.0	0.20	55	25 (26)
6.0	0.25	55	23 (23)
6.0	0.30	55	20 (21)
6.0	0.40	55	17.3 (17.8)
6.0	0.55	55	14.7 (15.0)
6.0	0.55	0.060	5.9 (6.2)
6.0	0.55	0.25	6.0 (6.2)
6.0	0.55	0.50	6.4 (6.3)
6.0	0.55	1.0	6.6 (6.4)
6.0	0.55	2.5	7.0 (6.6)
6.0	0.55	5.0	7.8 (7.0)
6.0	0.55	20	9.2 (9.5)
6.0	0.55	30	11.2 (11.1)

[a]Reactions at 22 °C, μ = 0.55 M (HCl/LiCl); λ = 430 nm. Generation of intermediate was too rapid to allow collection of kinetic data. [b]First order rate constants; parenthetical values were calculated from eq. (11) in text, using parameters in Table 3.

Table S-6 – The Mo(VI)-Ti(III) reaction; decay of the Mo(V) transient. Kinetic data[a]

[Ti(III)], mM	$[H^+]$, M	$[Cl^-]$, M	k_{obsd}, s^{-1} [b]
2.5	0.50	0.50	3.3 (3.6)
3.0	0.50	0.50	3.8 (4.0)
3.8	0.50	0.50	4.4 (4.6)
5.0	0.50	0.50	5.1 (5.3)
6.3	0.50	0.50	6.0 (5.9)
7.5	0.50	0.50	6.4 (6.4)
3.0	0.10	0.50	0.74 (0.80)
3.0	0.15	0.50	1.15 (1.20)
3.0	0.20	0.50	1.47 (1.61)
3.0	0.25	0.50	2.0 (2.0)
3.0	0.40	0.50	3.5 (3.2)
3.0	0.45	0.50	3.9 (3.6)
3.0	0.50	0.15	1.32 (1.21)
3.0	0.50	0.20	1.78 (1.61)
3.0	0.50	0.25	2.4 (2.0)
3.0	0.50	0.40	3.6 (3.2)
3.0	0.50	0.45	3.8 (3.6)
3.0	0.50	0.50	3.9 (4.0)

[a]Reactions at 22 °C; μ = 0.50 M (HCl/LiCl); λ = 430 nm. [b]First order rate constants; parenthetical values were calculated from eq. (12) in text, using parameters in Table