Reactions of vanadium(IV) and –(V) with s^2 metal-ion reducing centers

Zhiyong Yang and Edwin S. Gould

SUPPLEMENTARY MATERIALS

S1. Stoichiometries of reduction of vanadium(V) and –V by s^2 metal centers

S2-S6 Kinetic data for redox reactions

Table S1. Stoichiometries of reduction of vanadium(V) and –(IV) by s^2-metal centers[a]

A. <u>Reductions of vanadium(V)[b]</u>

Reductant	[Red], mM	[Ox], mM	Δ[Ox], mM	Δ[Ox]/Δ[red]
In(I)[c]	0.15	1.50	0.29	1.93
	0.30	1.50	0.58	1.92
	0.56	1.50	1.08	1.93
Ge(II)[d]	0.073	1.00	0.140	1.92
	0.147	1.00	0.28	1.91
	0.367	1.00	0.70	1.91
Sn(II)[d]	0.146	1.00	0.28	1.93
	0.290	1.00	0.57	1.98
	0.367	1.00	0.71	1.95

B. <u>Reductions of vanadium(IV)[e]</u>

Reductant	[Red], mM	[Ox], mM	Δ[Ox], mM	Δ[Ox]/Δ[red]
In(I)[f]	1.93	9.97	3.95	2.05
	2.90	14.7	5.90	2.04
	3.87	14.7	7.86	2.03
Ge(II)[g]	3.00	14.3	6.25	2.08[h]
	3.00	28.7	6.23	2.08[h]
	6.00	57.3	12.1	2.01
	12.0	57.3	23.2	1.93
Sn(II)[i]	13.8	37.7	28.4	2.07
	23.0	56.0	47.8	2.08
	13.8	39.7	28.3	2.06[h]
	18.4	48.2	38.6	2.09[h]

[a]Reactions at 22 °C. [b]Added as ammonium vanadate; λ = 280 nm. [c]Reactions in 0.33 M NaClO$_4$ + 0.016 M HClO$_4$. [d]0.17 M HCl + 0.33 M NaCl. [e]Added as VO(ClO$_4$)$_2$; λ = 760 nm. [f]HAc/Ac buffer (pH 4.70). [g]2.0 M HCl, [Cu^{2+}] = 1.0 mM. [h][Cu^{2+}] = 2.2 mM. [i]4.0 M HCl, [Cu^{2+}] = 1.0 mM.

Table S2. Kinetic data for reduction of vanadium(V) with tin(II)[a]

$[H^+]$, M	$[Cl^-]$, M	$[Sn^{2+}]$, mM	$10^{-3}k$, $M^{-1}s^{-1}$ [b]
0.40	0.20	1.25	0.48 (0.44)
0.40	0.30	1.25	0.91 (0.90)
0.40	0.40	1.25	1.38 (1.42)
0.40	0.50	1.25	1.94 (1.95)
0.40	0.60	1.25	2.41 (2.47)
0.40	0.70	1.25	2.9 (3.0)
0.40	0.80	1.25	3.4 (3.5)
0.40	0.90	1.25	3.8 (3.9)
0.40	1.00	1.25	4.4 (4.4)
0.50	1.00	1.25	5.5 (5.5)
0.50	1.00	2.50	5.5 (5.5)
0.50	1.00	5.05	5.6 (5.5)
0.60	1.00	1.25	6.6 (6.6)
0.70	1.00	1.25	7.7 (7.7)
0.80	1.00	1.25	8.8 (8.8)
0.90	1.00	1.25	9.8 (9.6)
1.00	1.00	1.25	10.2 (10.6)
1.00	1.00	1.25	9.9[c]

[a]Reactions were carried out at 22.0 ± 0.5 °C; μ = 1.0 M (HCl/NaCl or HClO$_4$/NaCl/NaClO$_4$); $[V^V]$ = 0.24 mM throughout; λ = 280 nm. [b]Parenthetical values calculated using eq. (7) and parameters listed in Table 7. [c]Cu(II) (1.0 mM) added.

Table S3. The reduction of vanadium(IV) by indium(I)[a]

pH	[V(IV)], mM	[In(I)], mM	k, $M^{-1}s^{-1}$
1.85	14.7	2.0	0.88^b (0.81)
2.10	14.7	2.0	0.88^b (0.88)
3.62	14.7	2.0	3.3 (3.3)
4.12	14.7	2.0	5.0 (4.7)
4.52	14.7	2.0	5.5 (5.5)
4.65	8.80	1.75	5.7 (5.6)
4.65	14.7	1.75	5.6 (5.6)
4.65	22.0	1.75	5.6 (5.6)
4.65	29.3	1.75	5.5 (5.6)
4.65	14.7	1.75	5.4^c

[a]Reactions were run at 22.0 ± 0.5 ^{o}C, $\mu = 0.20$ M (ClO$_4^-$/acetate); $\lambda = 760$ nm; [CH$_3$CN] =

0.13 M [b]H$_3$PO$_4$/H$_2$PO$_4^-$ buffer. [c][CH$_3$CN] = 1.43 M.

Table S4 – Reduction of vanadium(IV) by germanium(II) as catalyzed by copper; kinetic data[a]

$[V^{IV}]$, mM	$[Cu^{II}]$, mM	$[H^+]$, M	10^2k, $M^{-1}s^{-1}$ [b]
57	1.00	0.50	17.5 (17.6)
57	1.00	0.83	26 (25)
57	1.00	1.33	35 (35)
57	1.00	1.67	41 (42)
57	1.00	2.00	53 (49)
57	0.020	2.00	6.4 (6.7)
57	0.10	2.00	11.8 (15.2)
57	0.20	2.00	22 (22)
57	0.46	2.00	36 (33)
57	0.50	2.00	40 (34)
15	0.91	2.00	43 (46)
30	0.91	2.00	45 (46)
44	0.91	2.00	41 (46)
58	0.91	2.00	43 (46)
57	2.0	2.00	80 (69)
57	0	2.0	<0.3[c]

[a]Reactions were carried out at 22.5 ± 0.5 ^{o}C; $[Ge^{II}]$ = 2.5 mM; μ = 2.0 M (HCl/NaCl); λ =

760 nm. [b]Second order rate constants calculated from initial rates (= $[rate]_o/[V]_o[Ge]_o$;

parenthetical values were calculated using expression (9) and parameters listed in Table 7.

[c]Upper limit in 2 M HCl.

Table S5. Kinetic data for the reduction of V(IV) with excess Sn(II) as catalyzed by copper[a]

$[H^+]$ (M)	$[Cl^-]$ (M)	$[Cu]$ (mM)	$[Sn^{II}]$ (mM)	k_{obs}[b] x 10^3 (s^{-1})	$[H^+]$ (M)	$[Cl^-]$ (M)	$[Cu]$ (mM)	$[Sn^{II}]$ (mM)	k_{obs}[b] x 10^3 (s^{-1})
0.50	4.0	0.50	64	0.67 (0.67)	4.0	4.0	0.025	64	0.28 (0.27)
0.90	4.0	0.50	64	1.25 (1.21)	4.0	4.0	0.10	64	1.11 (1.08)
1.3	4.0	0.50	64	1.59 (1.75)	4.0	4.0	0.40	64	4.4 (4.3)
1.7	4.0	0.50	64	1.90 (2.29)	4.0	4.0	0.60	64	7.0 (6.5)
2.5	4.0	0.50	64	2.9 (3.4)	4.0	4.0	0.80	64	8.9 (8.6)
3.3	4.0	0.50	64	4.0 (4.4)	4.0	4.0	1.0	64	11.0 (10.8)
4.0	4.0	0.50	64	5.6 (5.4)	4.0	4.0	0.50	16[c]	5.1 (5.4)
4.0	0.30	0.50	64	3.4 (3.9)	4.0	4.0	0.50	32[c]	5.0 (5.4)
4.0	0.50	0.50	64	4.8 (4.2)	4.0	4.0	0.50	64[c]	5.2 (5.4)
4.0	0.90	0.50	64	5.5 (4.6)	4.0	4.0	0.50	128[c]	5.3 (5.4)
4.0	2.5	0.50	64	6.6 (5.2)					
4.0	3.2	0.50	64	5.9 (5.3)					

[a]Reactions run at 22 ± 0.5 °C, μ = 4.0 M (HCl/NaCl; or NaCl/HClO$_4$/NaClO$_4$), λ = 760 nm, $[V^{IV}]$ = 5.0 mM unless otherwise indicated. [b]Parenthetical values calculated using expression (10) and kinetic parameters in Table 7. [c]$[V^{IV}]$ = 5.0 mM.

Table S6. The reduction of Cu(II) with Sn(II) at high [Cl⁻][a]

[H$^+$], M	$10^{-2}k$, M^{-1}s^{-1}
0.80	1.84 ± 0.10
1.60	3.9 ± 0.2
2.40	4.5 ± 0.3
4.0	7.1 ± 0.6

[a]Reactions carried out at 23 $^{\circ}$C, λ = 880 nm, μ = 4.0 M (HCl/LiCl); [Sn^{II}] = 23.0 mM; [Cu^{II}] = 4.1 mM.