Kinetics of complexation of V(V), U(VI), and Fe(III) with glutaroidime-dioxime: studies by stopped-flow and conventional absorption spectroscopy

Bernard F. Parker,1,2 Zhicheng Zhang,2 Christina J. Leggett,2,3 John Arnold,1,2 Linfeng Rao2,*

1Department of Chemistry, University of California – Berkeley, Berkeley, CA 94720, USA
2Chemical Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, CA 94720, USA
3U. S. Nuclear Regulatory Commission, 11545 Rockville Pike, Rockville, MD 20852, USA

Electronic Supporting Information

Additional spectra and kinetic traces

Vanadium

Figure S1: Sample curves for the formation of complex 1 from stopped-flow kinetic experiments showing the effect of ligand concentration. Conditions: [V] = 0.200 mM, pH = 8.
Figure S2: Sample curves for the formation of complex 1 from stopped-flow kinetic experiments showing the effect of vanadium concentration. Conditions: [L] = 0.500 mM, pH = 8.

Figure S3: Spectra monitoring the formation of 2 over time by conventional UV-Vis spectroscopy. Conditions: [V] = 0.200 mM; [L] = 0.500 mM. The number of spectra shown has been reduced for clarity.
Figure S4: $^{51}$V NMR spectra monitoring speciation of a V/L mixture over time (see Figure 5a in the main text). Conditions; [V] = 3 mM, [L] = 6 mM, pH = 7-8.

Figure S5: $^1$H NMR spectra monitoring speciation of a V/L mixture over time (see figure 5b in the main text). Conditions; [V] = 3 mM, [L] = 6 mM, pH = 7-8.
Figure S6: $^{51}V$ speciation of a V/L mixture changing over time. Conditions; [V] = 6 mM, [L] = 6 mM, pH = 7-8. Uncertainties of measurements are estimated to be < ±5%.

Figure S7: $^1H$ speciation of a V/L mixture changing over time (note: [VL] and [VL2] ratio determined from $^{51}V$ NMR due to overlap in the $^1H$ spectra; see Figure S9). Conditions; [V] = 6 mM, [L] = 6 mM, pH = 7-8. Uncertainties of measurements are estimated to be < ±5%.
Figure S8: $^{51}$V NMR spectra monitoring speciation of a V/L mixture over time (see figure S6). Conditions; [V] = 6 mM, [L] = 6 mM, pH = 7-8.

Figure S9: $^1$H NMR spectra monitoring speciation of a V/L mixture over time (see figure S7). Conditions; [V] = 6 mM, [L] = 6 mM, pH = 7-8.
Figure S10: $^{51}$V speciation of a V/L mixture changing over time. Conditions; [V] = 12 mM, [L] = 6 mM, pH = 7-8. $^1$H speciation (starting at 1 day) shows only VL.

Figure S11: $^{51}$V NMR spectra monitoring speciation of a V/L mixture over time (see figure S10). Conditions; [V] = 12 mM, [L] = 6 mM, pH = 7-8. No changes were observed after 3 days, and no signals were observed at δ > -300 ppm.
Figure S12: Spectra monitoring the formation of 4 over time. Conditions: [UO$_2$] = 0.200 mM, [L] = 0.500 mM, [CO$_3$] = 1.200 mM, [Ca] = 2.50 mM, pH = 7. The number of spectra shown has been reduced for clarity (t = 0.1s to t = 8.0 s)

Figure S13: Sample curves from stopped-flow kinetic experiments showing the effect of ligand concentration. Conditions: [UO$_2$] = 0.200 mM, [carbonate] = 1.600 mM, [Ca] = 2.50 mM, pH = 7.
Figure S14: Sample curves from stopped-flow kinetic experiments showing the effect of uranyl concentration. Conditions: [L] = 0.500 mM, [carbonate] = 25×[UO₂], [Ca] = 25×[U], pH = 7.

Figure S15: Sample curves from stopped-flow kinetic experiments showing the effect of carbonate concentration. Note that two distinct slopes are only visible at the lowest [carbonate]. Conditions: [UO₂] = 0.200 mM, [Ca] = 2.50 mM, pH = 7.
Iron

**Figure S16:** Spectra monitoring the formation of 3 over time. Conditions: [Fe] = 0.200 mM; [L] = 0.500 mM. The number of spectra shown has been reduced for clarity (t = 0.2 s to t = 20.0 s)

**Figure S17:** Sample curves from stopped-flow kinetic experiments showing the effect of ligand concentration. Conditions: [Fe] = 0.200 mM, pH = 4.5.
Figure S18: Sample curves from stopped-flow kinetic experiments showing the effect of iron concentration. Conditions: [L] = 0.500 mM, pH = 4.5.
Speciation diagrams

Figure S19: Speciation of 0.2 mM V(V) in the absence (upper) and presence of 0.5 mM glutaroiomide-dioxime (lower), for the stopped-flow experiments monitoring the formation of 1:1 V/L complex. The equilibrium constants of V(V) alone are taken from L.Pettersson and K.Elvingson, Vanadium Compounds, 1998, vol. 711, pp. 30–50. The V/L complexation constants are taken from an unpublished thermodynamic study from our group.
Figure S20: Speciation of 0.2 mM U(VI) in the absence (upper) and presence of 0.5 mM glutaroimide-dioxime (lower). $C_{\text{carbonate}} = 0.6$ mM, $C_{\text{Ca}} = 2.5$ mM. The hydrolysis constants of U(VI) are taken from I. Grenthe et al., “Chemical Thermodynamics of Uranium”. The U/L complexation constants are taken from ref.11 of the main text.
Figure S21: Speciation of 0.2 mM Fe(III) in the absence (upper) and presence of 0.5 mM glutaroimide-dioxime (lower). In the absence of glutaroimide-dioxime, Fe(OH)$_3$ that is formed will precipitate, driving the equilibrium to forming more Fe(OH)$_3$, and so the speciation and mass balance are only accurate up to pH = 4. The hydrolysis constants of Fe(III) are taken from C.F.Baes, Jr. and R.E.Mesmer, “The Hydrolysis of Cations”. The Fe/L complexation constants are taken from ref.13 of the main text.