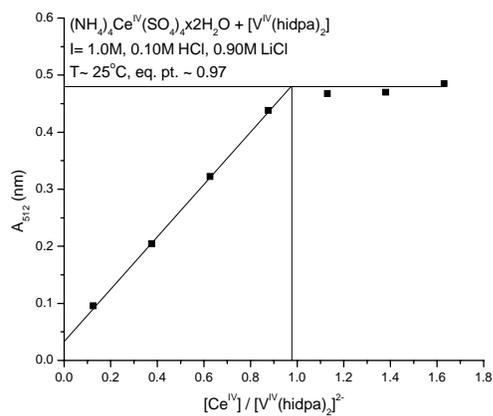
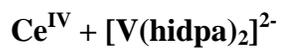


Supplemental Information
Kinetics of electron transfer of Ce^{IV} + $[\text{V}(\text{hidpa})_2]^{2-}$

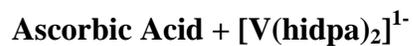
Stoichiometric equivalence points

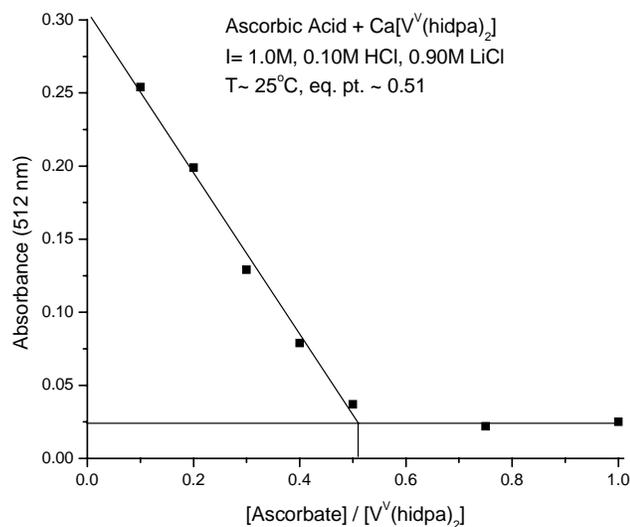


| $[\text{V}(\text{hidpa})_2]^{2-} + \text{Ce}(\text{IV})$ | |
|--|---------|
| Equivalence Point | Average |
| 0.97 | 0.97 |
| 0.96 | |

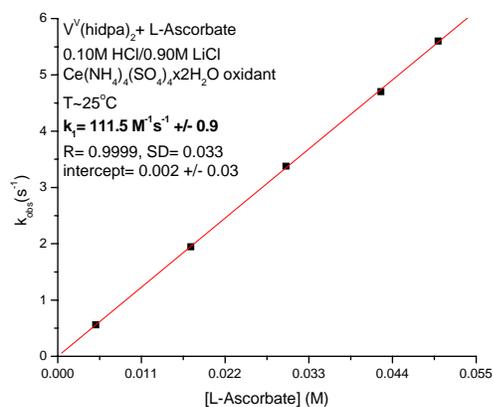


| $[\text{V}(\text{hidpa})_2]^{2-} + \text{K}_2\text{IrCl}_6$ | |
|---|---------|
| Equivalence Point | Average |
| 1.24 | 1.1 |
| 1.14 | |
| 1.14 | |
| 1.14 | |
| 1.04 | |



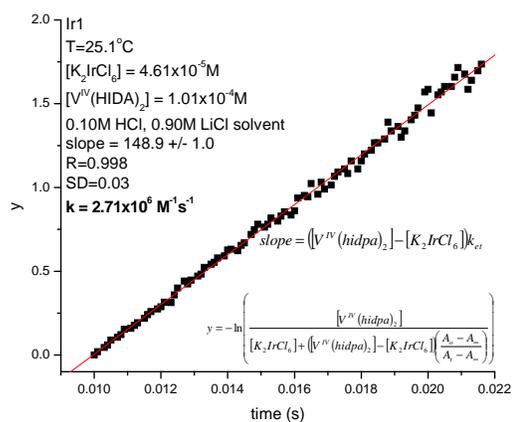
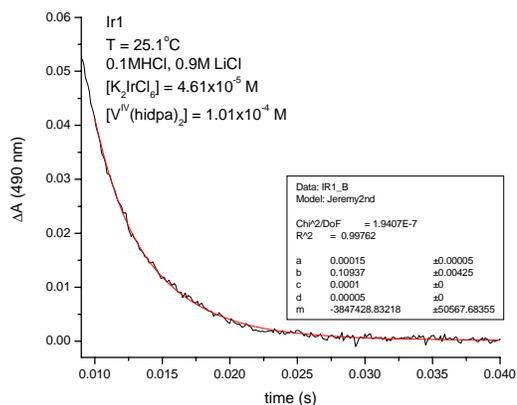


Kinetics
 Ascorbic Acid



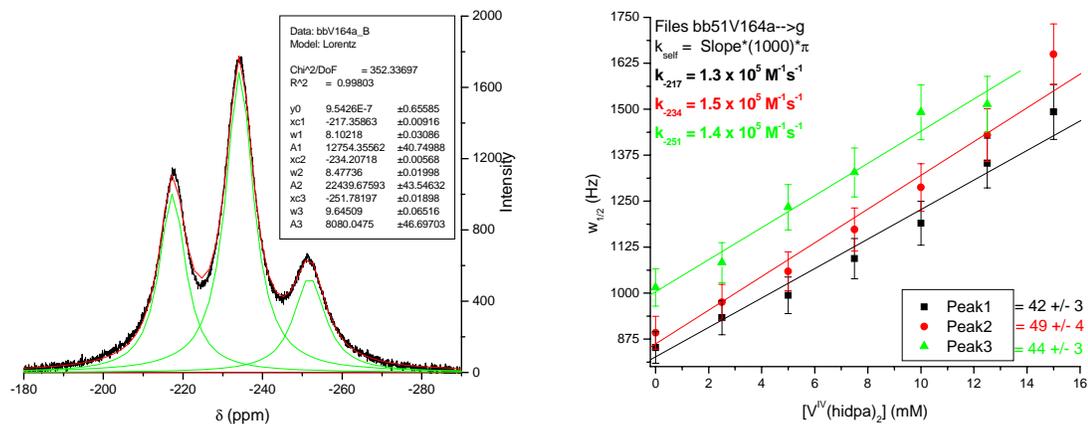
| [HCl] (M) | [L-Ascorbate] (M) | k (s ⁻¹) | k_{rxn} (M ⁻¹ s ⁻¹) |
|-----------|-------------------------|------------------------|---|
| 0.010 | 5.00 x 10 ⁻³ | 4.2 | 790 +/- 50 |
| 0.010 | 1.75 x 10 ⁻² | 14.5 | |
| 0.010 | 3.00 x 10 ⁻² | 27.4 | |
| 0.010 | 4.25 x 10 ⁻² | 34.5 | |
| 0.010 | 5.00 x 10 ⁻² | 39.1 | |
| 0.010 | 5.00 x 10 ⁻² | 4.7 | 870 +/- 31 |
| 0.010 | 1.75 x 10 ⁻² | 16.4 | |
| 0.010 | 3.00 x 10 ⁻² | 28.4 | |
| 0.010 | 4.25 x 10 ⁻² | 38.4 | |
| 0.010 | 5.00 x 10 ⁻² | 42.4 | |
| 0.017 | 5.00 x 10 ⁻³ | 2.9 | 590 +/- 6 |
| 0.017 | 1.75 x 10 ⁻² | 9.9 | |
| 0.017 | 3.00 x 10 ⁻² | 17.2 | |
| 0.017 | 4.25 x 10 ⁻² | 24.8 | |
| 0.017 | 5.00 x 10 ⁻² | 29.3 | |

| | | | |
|-------|-----------------------|------|-------------------|
| 0.025 | 5.00×10^{-3} | 2.0 | |
| 0.025 | 1.75×10^{-2} | 7.1 | |
| 0.025 | 3.00×10^{-2} | 12.3 | 420 +/- 5 |
| 0.025 | 4.25×10^{-2} | 17.4 | |
| 0.025 | 5.00×10^{-2} | 21.0 | |
| 0.050 | 5.00×10^{-3} | 1.0 | |
| 0.050 | 1.75×10^{-2} | 3.3 | |
| 0.050 | 3.00×10^{-2} | 5.8 | 190 +/- 12 |
| 0.050 | 4.25×10^{-2} | 7.6 | |
| 0.050 | 5.00×10^{-2} | 10.1 | |
| 0.10 | 5.00×10^{-3} | 0.6 | |
| 0.10 | 1.75×10^{-2} | 1.9 | |
| 0.10 | 3.00×10^{-2} | 3.4 | 110 +/- 1 |
| 0.10 | 4.25×10^{-2} | 4.7 | |
| 0.10 | 5.00×10^{-2} | 5.6 | |
| 0.50 | 5.00×10^{-3} | 0.1 | |
| 0.50 | 1.75×10^{-2} | 0.4 | |
| 0.50 | 3.00×10^{-2} | 0.8 | 26 +/- 1 |
| 0.50 | 4.25×10^{-2} | 1.1 | |
| 0.50 | 5.00×10^{-2} | 1.3 | |



| T = 25°C, 0.10 M HCl, 0.90 M LiCl | | | | |
|-----------------------------------|-----------------------|-----------------------------|-------------------------------------|-------------------------------------|
| $[K_2IrCl_6]$ (M) | $[V(hidpa)_2]^{2-}$ | k_{et} ($M^{-1}s^{-1}$) | k_{avg} ($M^{-1}s^{-1}$) | SD |
| 2.37×10^{-5} | 5.03×10^{-5} | 3.6×10^6 | | |
| 4.61×10^{-5} | 1.01×10^{-4} | 2.7×10^6 | | |
| 7.01×10^{-5} | 1.51×10^{-4} | 2.6×10^6 | | |
| 1.00×10^{-4} | 2.01×10^{-4} | 2.3×10^6 | | |
| 1.25×10^{-4} | 2.51×10^{-4} | 2.0×10^6 | 3.2×10^6 | 1.1×10^6 |
| 2.76×10^{-5} | 5.08×10^{-5} | 3.1×10^6 | | |
| 2.76×10^{-5} | 1.02×10^{-4} | 5.6×10^6 | | |
| 4.87×10^{-5} | 1.02×10^{-4} | 2.9×10^6 | | |
| 4.87×10^{-5} | 1.52×10^{-4} | 4.1×10^6 | | |

I. ^{51}V -NMR Line Broadening



| File | $k_{\text{self exchange}} (\text{M}^{-1} \text{s}^{-1})$ | | | | | Avg. | SD |
|----------|--|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| | 161 | 162 | 163 | 164 | 165 | | |
| -217 ppm | 1.2×10^5 | 1.3×10^5 | 1.1×10^5 | 1.3×10^5 | 1.0×10^4 | 1.0×10^5 | 5.2×10^4 |
| -234 ppm | 1.4×10^5 | 1.2×10^5 | 1.3×10^5 | 1.5×10^5 | 1.9×10^4 | 1.1×10^5 | 5.4×10^4 |
| -251 ppm | 1.5×10^5 | 1.1×10^5 | 1.6×10^5 | 1.3×10^5 | 3.5×10^4 | 1.2×10^5 | 5.0×10^4 |