SYNTHESIS OF A PYRIDINIUM BIS[CITRATO(2−)]OXOCHROMATE(V) COMPLEX AND ITS LIGAND-EXCHANGE REACTIONS

Supporting Information

Carissa M. Cawich, Amritha Ibrahim, Karen L. Link, Allan Bumgartner, Mata D. Patro and Surendra N. Mahapatro*

Department of Chemistry, Regis University, Denver, Colorado 80221

Peter A. Lay* and Aviva Levina,

Centre for Heavy Metals Research, School of Chemistry, University of Sydney, New South Wales 2006, Australia

Sandra S. Eaton* and Gareth R. Eaton

Department of Chemistry and Biochemistry, University of Denver, Denver, Colorado 80208

Table S1. Conditions Applied to the MS XAFS Fittings for the Cr(V)-Cr(III)-citrate mixture.[a]

Legs = 5
R_{max} = 5
PW = 2 %
CW = 3 %
XAFS range:[b] k = 0-16 Å^{-1}
FT range:[b] R' = 0.8-4.5 Å^{-1}
E_0 = –15 – 0,[c,d] eV
S_0^2 = 0.8 – 1.0[c,d]
$N_0 = N_i$ (i = 1-11)[e,f]
$N_{12} = N_j$ (j = 13-28)[e,f]
$E_0(0) - E_0(12) = 2.5 \pm 1$[c,f]
$\sigma_i^2 > 0.001 \pm 0.0005$ (Å^2; i = 1-11,13-21)[c,f]
$\sigma_i^2 < 0.01 \pm 0.001$ (Å^2; i = 1-11,13-21)[c,f]
$\sigma_j^2 > \sigma_i^2 + (0.001 \pm 0.0005)$ ($i = 2, j = 6$; $i = 3, j = 7$; $i = 6, j = 10$; $i = 13, j = 17$; $i = 14, j = 18$; $i = 17, j = 21$; $i = 23, j = 24$; $i = 24, j = 25$)[c,f]
$\sigma_j^2 = \sigma_i^2 \pm 0.001$ ($i = 2, j = 13$; $i = 3, j = 14$; $i = 4, j = 15$; $i = 5, j = 16$; $i = 6, j = 17$; $i = 7, j = 18$; $i = 10, j = 21$; $i = 13, j = 23$; $i = 17, j = 24$; $i = 21, j = 25$)[c,f]
$\sigma_j^2 = \sigma_i^2$ ($i = 2, j = 4$; $i = 3, j = 5$; $i = 6, j = 8$; $i = 7, j = 9$; $i = 10, j = 11$; $i = 13, j = 15$; $i = 14, j = 16$; $i = 17, j = 19$; $i = 18, j = 20$; $i = 21, j = 22$; $i = 23, j = 26$; $i = 24, j = 27$; $i = 25, j = 28$;)[e,f]

---

[a] Designations: *Legs* is the maximal number of legs in MS; R_{max} is the maximal effective pathlength of a photoelectron; *PW* is the plane-wave path filter threshold; *CW* is the curved-wave path filter threshold; $\Delta E_0 = E_0 - 6005$ eV is the threshold energy; S_0^2 is the scale factor; N are the occupancies; and σ^2 are the Debye-Waller factors. [b] Application of window functions is shown in Figure S1. [c] Restraint. [d] For both Cr atoms (0 and 12 in Chart S1). [e] Constraint. [f] Atom numbering corresponds to Chart S1.

Table S2. Initial, Restrained and Optimized Parameters of MS XAFS Fitting for the Cr(V)-Cr(III)-citrate mixture.

Parameter[a]	Initial	Restrained	Optimized
R, %	102	--	13.8
$N(0)$	0.50	*b*	0.26
$N(12)$	0.50	*b*	0.74
$E_0(0)$, eV	–7	*b*	–1.2
$E_0(12)$, eV	–9.5	*b*	–3.6
$S_0^2(0)$	0.90	*b*	0.91
$S_0^2(12)$	0.90	*b*	0.92
Bond Lengths,[c] Å			
12–0[d]	10.00	--	10.00
1–0	1.56	1.56	1.59
2–0	1.89	1.90	1.90
3–0	1.80	1.79	1.81
6–2	1.31	1.31	1.31
7–3	1.42	1.42	1.42
7–6	1.51	1.51	1.51
10–6	1.22	1.22	1.22
4–0	1.89	1.90	1.90
5–0	1.80	1.79	1.81
8–4	1.31	1.31	1.31
9–5	1.42	1.42	1.42
9–8	1.51	1.51	1.51
11–8	1.22	1.22	1.22
13–12	1.91	1.90	1.90
14–12	1.91	1.96[e]	1.99
17–13	1.35	1.31	1.31
18–14	1.43	1.42	1.42
18–17	1.51	1.51	1.51
21–17	1.22	1.22	1.21
15–12	1.91	1.90	1.90
16–12	1.91	1.96[e]	1.99
19–15	1.36	1.31	1.31
20–16	1.43	1.42	1.42
20–19	1.51	1.51	1.51
22–19	1.22	1.22	1.22
12–23	1.91	1.90	1.91
24–23	1.36	1.31	1.31
25–24	1.22	1.22	1.23
12–26	1.91	1.90	1.90
27–26	1.36	1.31	1.31
28–27	1.22	1.22	1.22
Bond Angles,[f] °			
1–0–2	102	--	108
1–0–3	114	--	117

Table S2 (continued).

Parameter[a]	Initial	Restrained	Optimized
1–0–4	101	--	109
1–0–5	114	--	116
2–0–3	83	--	94
4–0–5	83	--	94
2–0–4	156	--	142
3–0–5	132	--	127
0–2–6	116	--	100
0–3–7	119	--	107
0–4–8	115	--	101
0–5–9	118	--	94
2–6–7	114	120	120
3–7–6	107	110	110
2–6–10	122	115	115
7–6–10	124	120	120
4–8–9	114	115	115
8–9–5	107	110	110
4–8–11	122	120	120
9–8–11	123	120	120
23–12–26	180	--	179
23–12–13	90	--	105
23–12–14	90	--	104
23–12–15	87	--	80
23–12–16	92	--	105
13–12–14	88	--	87
15–12–16	88	--	94
13–12–15	177	--	175
14–12–16	177	--	150
12–13–17	107	--	110
12–14–18	108	--	107
12–15–19	107	--	99
12–16–20	108	--	100
13–17–18	116	120	120
14–18–17	106	110	110
13–17–21	122	120	120
18–17–21	122	120	120
15–19–20	116	120	120
19–20–16	106	110	110
15–19–22	121	120	120
20–19–22	121	120	120
23–24–25	116	120	120
26–27–28	126	120	120

[a] Designations correspond to Table S1; atom numbering corresponds to Chart S1.

[b] Conditions applied to these values are given in Table S1; calculated errors are given in Table 1. [c] Allowed deviations from the restrained values were ± 0.05 Å; errors (calculated by Monte-Carlo method)[53] did not exceed 0.01 Å, expected systematic errors 0.01-0.02 Å [9]. [d] Distance between the two Cr centres. [e] Allowed deviations from the restrained values were ± 0.1 Å. [f] Allowed deviations from the restrained values were ± 5°; errors (calculated by Monte-Carlo method)[53] did not exceed 1°, expected systematic errors 1-2°.[51]

Table S3. Most Significant Scattering Paths in the Calculated XAFS Spectrum for the Cr(V)-Cr(III)-Citrate Mixture [a]

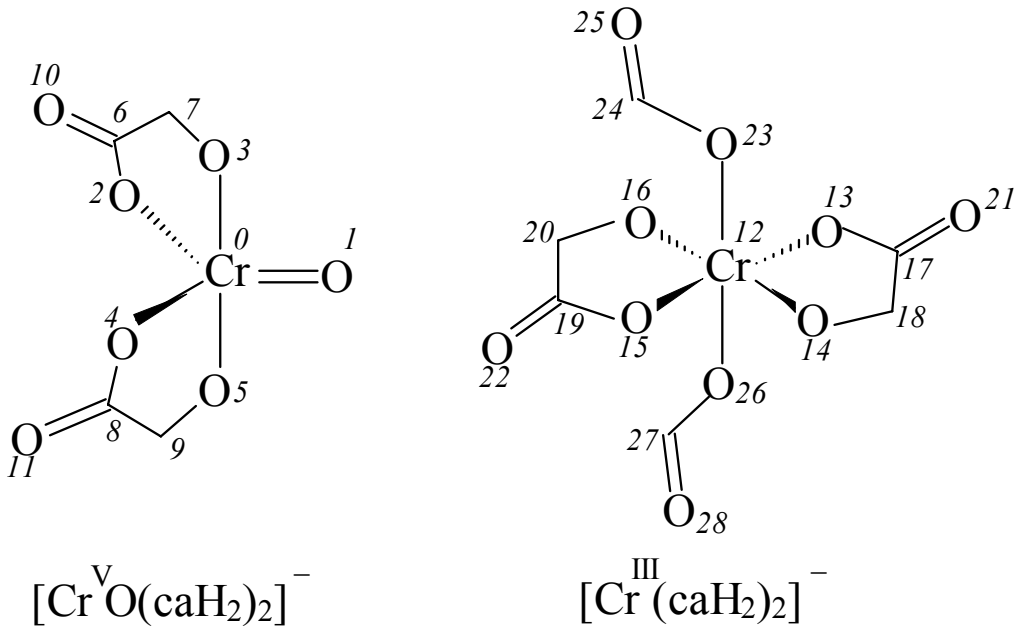
Path	Degeneracy	Length, Å	Contribution, %
2-Leg Paths			
$0 \rightarrow 1 \rightarrow 0$	1	1.591	100
$0 \rightarrow 3 \rightarrow 0$	1	1.813	69.8
$0 \rightarrow 5 \rightarrow 0$	1	1.815	69.6
$0 \rightarrow 2 \rightarrow 0$	2	1.899	100
$0 \rightarrow 6 \rightarrow 0$	1	2.582	20.0
$0 \rightarrow 7 \rightarrow 0$	1	2.662	18.0
$0 \rightarrow 8 \rightarrow 0$	1	2.697	19.6
$0 \rightarrow 9 \rightarrow 0$	1	2.723	17.0
$0 \rightarrow 10 \rightarrow 0$	1	3.635	9.9
$0 \rightarrow 11 \rightarrow 0$	1	3.818	7.5
$12 \rightarrow 13 \rightarrow 12$	1	1.896	100
$12 \rightarrow 26 \rightarrow 12$	1	1.901	100
$12 \rightarrow 15 \rightarrow 12$	1	1.902	59.2
$12 \rightarrow 23 \rightarrow 12$	1	1.912	60.1
$12 \rightarrow 14 \rightarrow 12$	1	1.993	63.3
$12 \rightarrow 16 \rightarrow 12$	1	1.995	63.2
$12 \rightarrow 27 \rightarrow 12$	1	2.349	24.9
$12 \rightarrow 24 \rightarrow 12$	1	2.499	20.6
$12 \rightarrow 19 \rightarrow 12$	1	2.540	20.9
$12 \rightarrow 17 \rightarrow 12$	1	2.745	15.4
$12 \rightarrow 20 \rightarrow 12$	1	2.756	13.3
$12 \rightarrow 18 \rightarrow 12$	1	2.890	9.64
3-Leg Paths			
$0 \rightarrow 6 \rightarrow 2 \rightarrow 0$	2	2.895	10.4
$0 \rightarrow 7 \rightarrow 3 \rightarrow 0$	2	2.950	11.0
$0 \rightarrow 8 \rightarrow 4 \rightarrow 0$	2	2.953	13.3
$0 \rightarrow 9 \rightarrow 5 \rightarrow 0$	2	2.981	11.9
$0 \rightarrow 5 \rightarrow 1 \rightarrow 0$	2	3.153	9.5
$0 \rightarrow 3 \rightarrow 1 \rightarrow 0$	2	3.174	10.6
$0 \rightarrow 10 \rightarrow 6 \rightarrow 0$	2	3.719	13.3
$0 \rightarrow 4 \rightarrow 2 \rightarrow 0$	2	3.751	14.3
$0 \rightarrow 11 \rightarrow 8 \rightarrow 0$	2	3.868	16.5
$12 \rightarrow 27 \rightarrow 26 \rightarrow 12$	2	2.777	12.2
$12 \rightarrow 24 \rightarrow 23 \rightarrow 12$	2	2.849	9.3
$12 \rightarrow 19 \rightarrow 15 \rightarrow 12$	2	2.875	9.8
$12 \rightarrow 17 \rightarrow 13 \rightarrow 12$	2	2.986	10.6
$12 \rightarrow 28 \rightarrow 27 \rightarrow 12$	2	3.574	30.7
$12 \rightarrow 25 \rightarrow 24 \rightarrow 12$	2	3.649	28.5
$12 \rightarrow 22 \rightarrow 19 \rightarrow 12$	2	3.705	17.1
$12 \rightarrow 23 \rightarrow 26 \rightarrow 12$	2	3.785	23.4
$12 \rightarrow 25 \rightarrow 23 \rightarrow 12$	2	3.828	10.3

$12 \rightarrow 21 \rightarrow 17 \rightarrow 12$	2	3.946	12.9

Table S3 (end).

Path	Degeneracy	Length, Å	Contribution, %
4-Leg Paths			
$0 \rightarrow 1 \rightarrow 0 \rightarrow 1 \rightarrow 0$	1	3.181	7.5
$0 \rightarrow 4 \rightarrow 0 \rightarrow 2 \rightarrow 0$	2	3.798	14.3
$0 \rightarrow 8 \rightarrow 11 \rightarrow 8 \rightarrow 0$	1	3.917	7.4
$0 \rightarrow 8 \rightarrow 11 \rightarrow 4 \rightarrow 0$	2	4.004	9.3
$12 \rightarrow 27 \rightarrow 28 \rightarrow 27 \rightarrow 12$	1	3.577	18.5
$12 \rightarrow 24 \rightarrow 25 \rightarrow 24 \rightarrow 12$	1	3.716	19.0
$12 \rightarrow 23 \rightarrow 12 \rightarrow 26 \rightarrow 12$	2	3.786	31.7
$12 \rightarrow 14 \rightarrow 12 \rightarrow 16 \rightarrow 12$	2	4.005	11.6
5-Leg Paths			
$12 \rightarrow 27 \rightarrow 28 \rightarrow 27 \rightarrow 26 \rightarrow 12$	2	4.005	11.6
$12 \rightarrow 24 \rightarrow 25 \rightarrow 24 \rightarrow 23 \rightarrow 12$	2	4.062	12.3

[a] Optimized XAFS parameters are given in Table 1 (main text) and Table S2 . Numbering of the atoms correspond to Chart S1. Contributions of the scattering paths were estimated in *FEFF 6.01* theory,[54] taking into account Debye-Waller factors of the atoms.[53] The maximum number of legs for the path was set to five. All the paths with significance ≥2% (total 283 paths) were used in the XAFS calculations.



$[Cr^{V}O(caH_2)_2]^-$ $[Cr^{III}(caH_2)_2]^-$

Chart S1. Model used for MS XAFS calculations for the Cr(V)-Cr(III)-citrate mixture. Atom numbering corresponds to that in Tables S1 and S2.

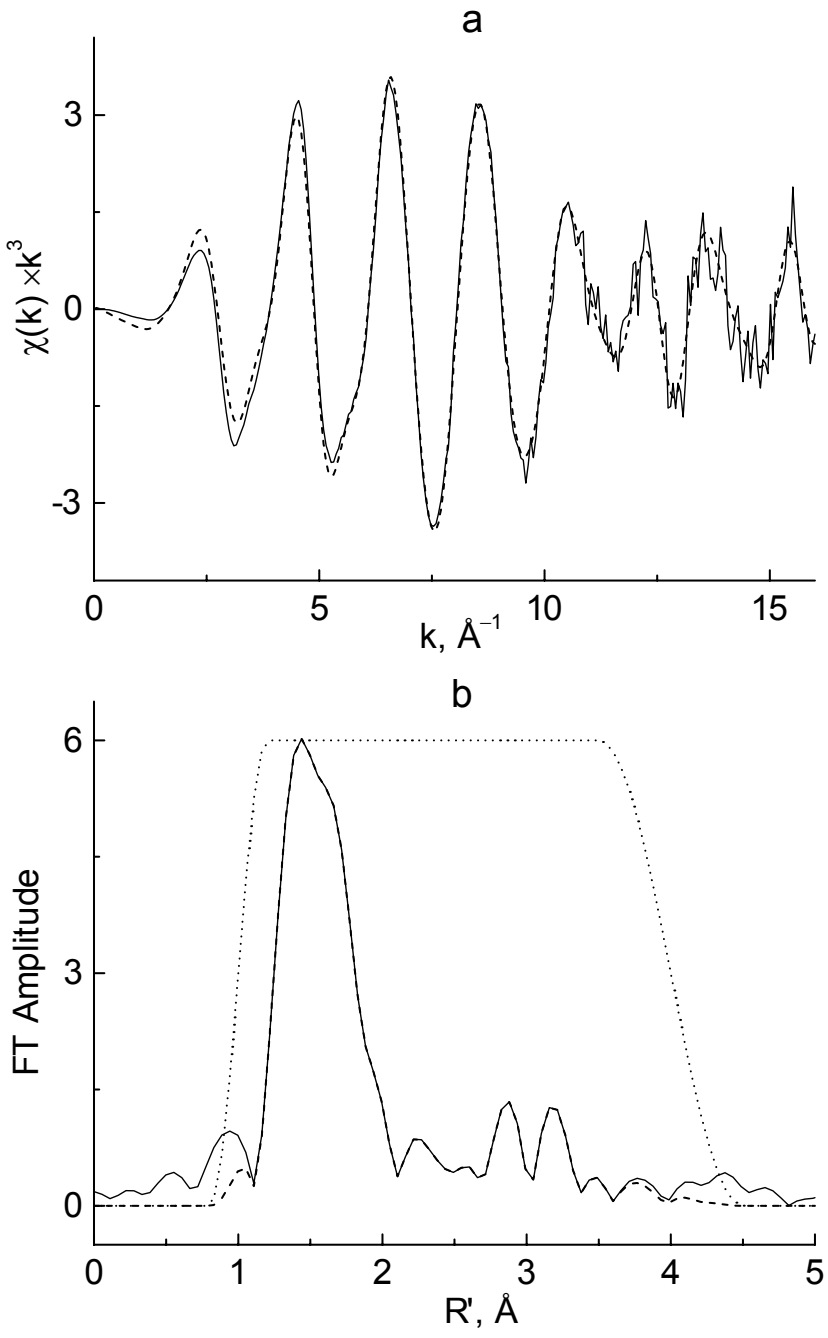


Figure S1. Application of window functions to MS XAFS calculations for the Cr(V)-Cr(III)-citrate mixture; **a:** experimental (solid lines) and Fourier-filtered (dashed lines) XAFS spectra; **b:** unwindowed (solid lines) and windowed (dashed lines) FT XAFS spectra, and window functions (dotted lines).

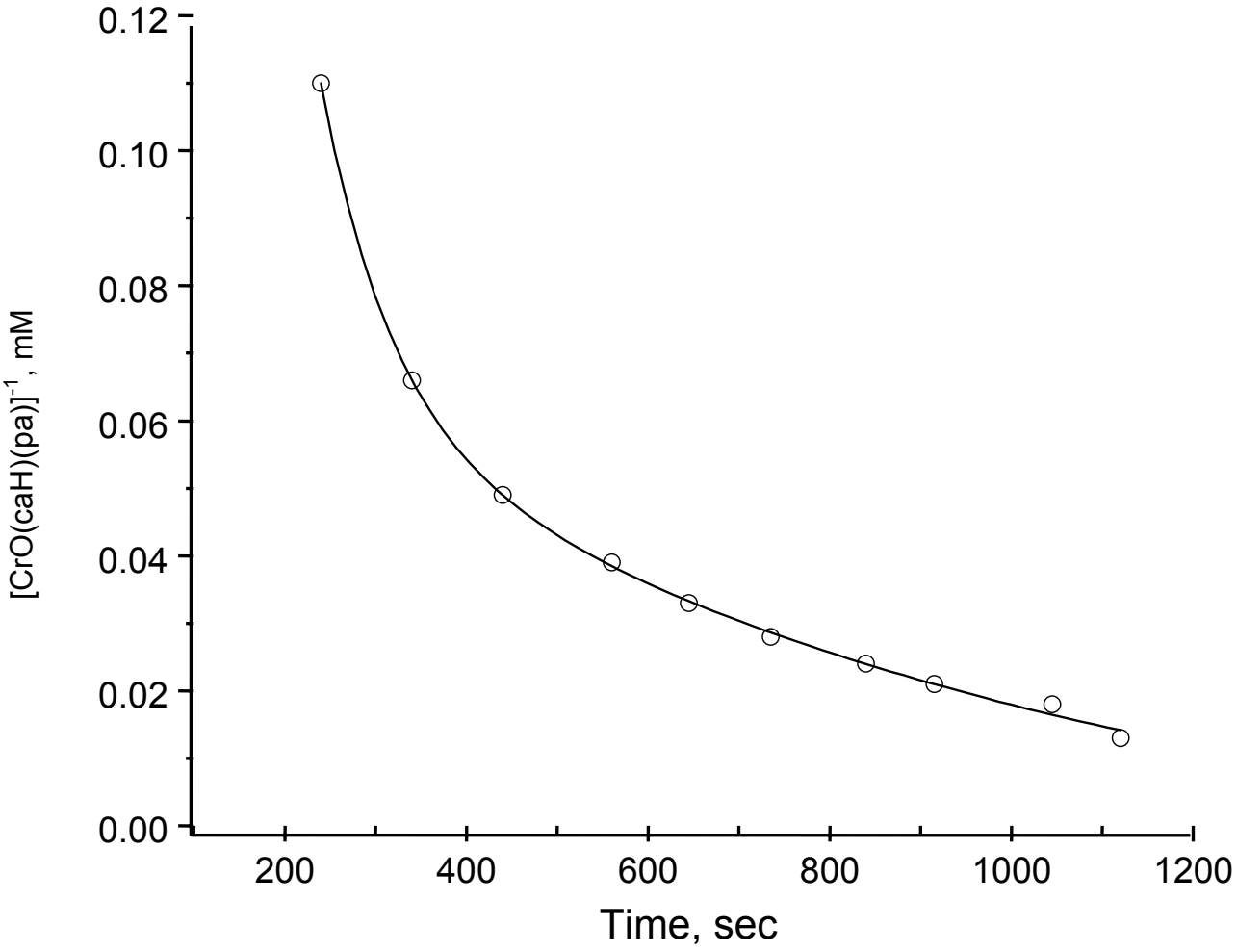
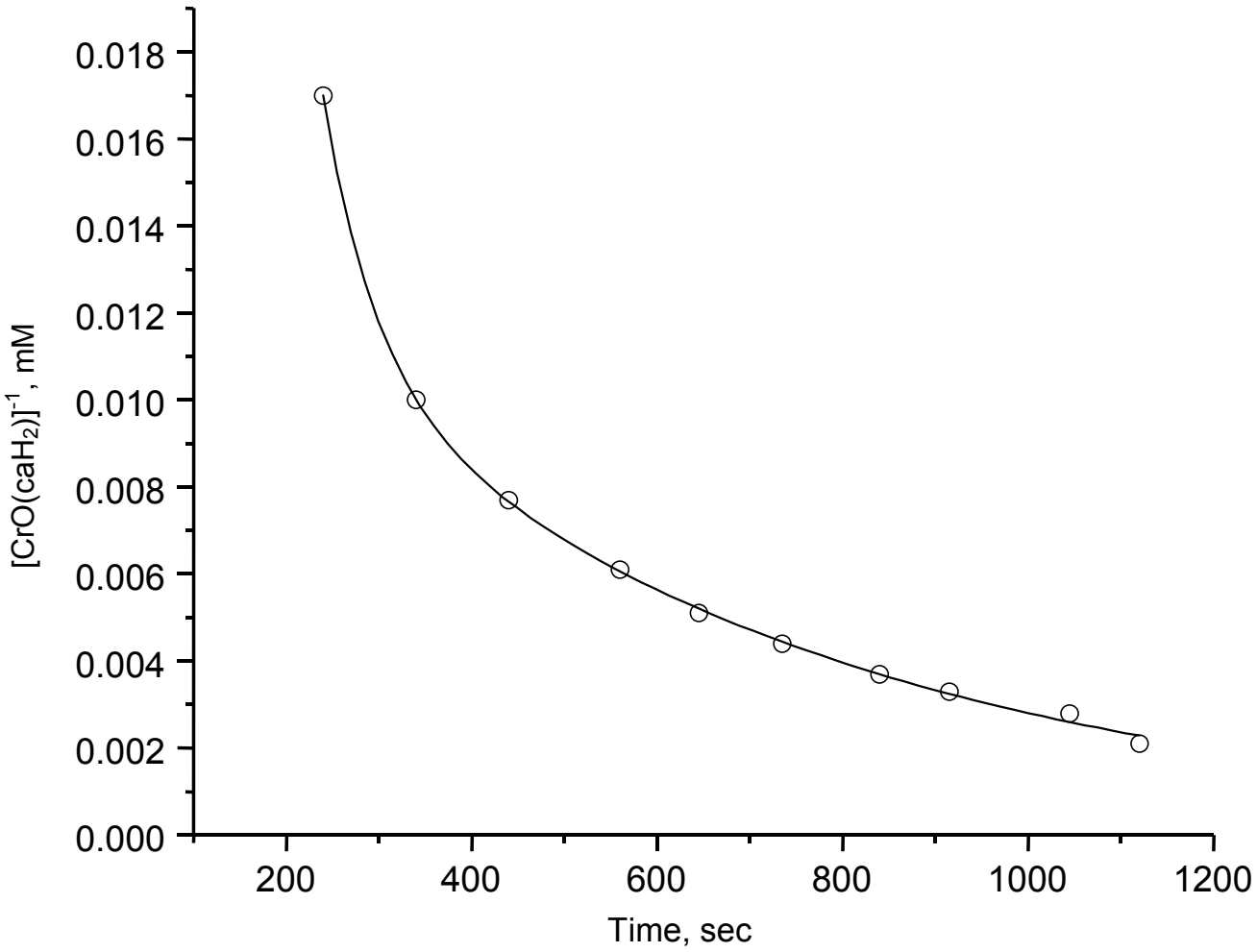


Figure S2: Decomposition of $[CrO(caH)(pa)]^{-1}$ fitted to two consecutive first order reactions



Chi^2/DoF= 1.8948E-8 R^2 = 0.99948 k_1 0.01768±0.00392 s^{-1} k_2 0.00182±0.00044 s^{-1}

Figure S3: Decomposition of $[CrO(CaH_2)_2]^{-1}$ fitted to two consecutive first order reactions