Vanadium(V) Oxoanions in Basic Water Solution: a Simple Oxidative System for the One Pot Selective Conversion of L-Proline to Pyrroline-2-Carboxylate

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SUPPORTING INFORMATION

Table S1. Selected standard reduction potentials for V(V), Cr(VI) and Mn(VII) oxoions in aqueous solution.

Reaction (acidic solution)		E° vs. SHE (298 K)	Ref.
Eq. (S1)	$[VO_2^+{}_{(aq)} + 2\ H^+{}_{(aq)} + e^- \rightarrow [VO]^{2+}{}_{(aq)} + H_2O$	+ 1.00 V	[1]
Eq. (S2)	$[Cr_2O_7^{2-}{}_{(aq)} + 14\ H^+{}_{(aq)} + 6\ e^- \rightarrow 2\ Cr^{3+}{}_{(aq)} + 7\ H_2O$	+ 1.33 V	[2]
Eq. (S3)	$[MnO_4^-{}_{(aq)} + 8\ H^+{}_{(aq)} + 5\ e^- \rightarrow Mn^{2+}{}_{(aq)} + 4\ H_2O$	+ 1.51 V	[2]
Reaction (basic solution)		**E° vs. SHE (298 K)**	**Ref**
Eq. (S4)	$2\ [VO_4^{3-}{}_{(aq)} + 7\ H^+{}_{(aq)} + 2\ e^- \rightarrow [HV_2O_5]^-{}_{(aq)} + 3\ H_2O$	+ 2.19 V	[1]
Eq. (S5)	$2\ [VO_4^{3-}{}_{(aq)} + 4\ H_2O + 2\ e^- \rightarrow [HV_2O_5]^-{}_{(aq)} + 7\ OH^-{}_{(aq)}$	− 0.70 V	[3]
Eq. (S6)	$[CrO_4^{2-}{}_{(aq)} + 4\ H_2O + 3\ e^- \rightarrow Cr(OH)_{3(s)} + 5\ OH^-{}_{(aq)}$	− 0.13 V	[4]
Eq. (S7)	$[MnO_4^-{}_{(aq)} + 2\ H_2O + 3e^- \rightarrow MnO_{2(s)} + 4\ OH^-{}_{(aq)}$	+ 1.23 V	[2]

[1] K. Post, R. G. Robins, *Electrochim. Acta*, 1976, **21**, 401-405.

[2] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements (Second Edition),* Butterworth-Heinemann, Oxford, 1997.

[3] Reduction potential calculated for Eq. (S4) at pH = 14 and formally corresponding to the standard reduction potential for Eq. (S5).

[4] A. F. Holleman, E. Wiberg, N. Wiberg, *Inorganic Chemistry*, San Diego 2001, Academic Press.

Figure S1. X-ray powder diffraction pattern of the black precipitate obtained from L-proline/NH$_4$VO$_3$ (black line), and calculated pattern of an equimolar mixture of (NH$_4$)$_2$V$_3$O$_8$ and NH$_4$VO$_3$ (red line).
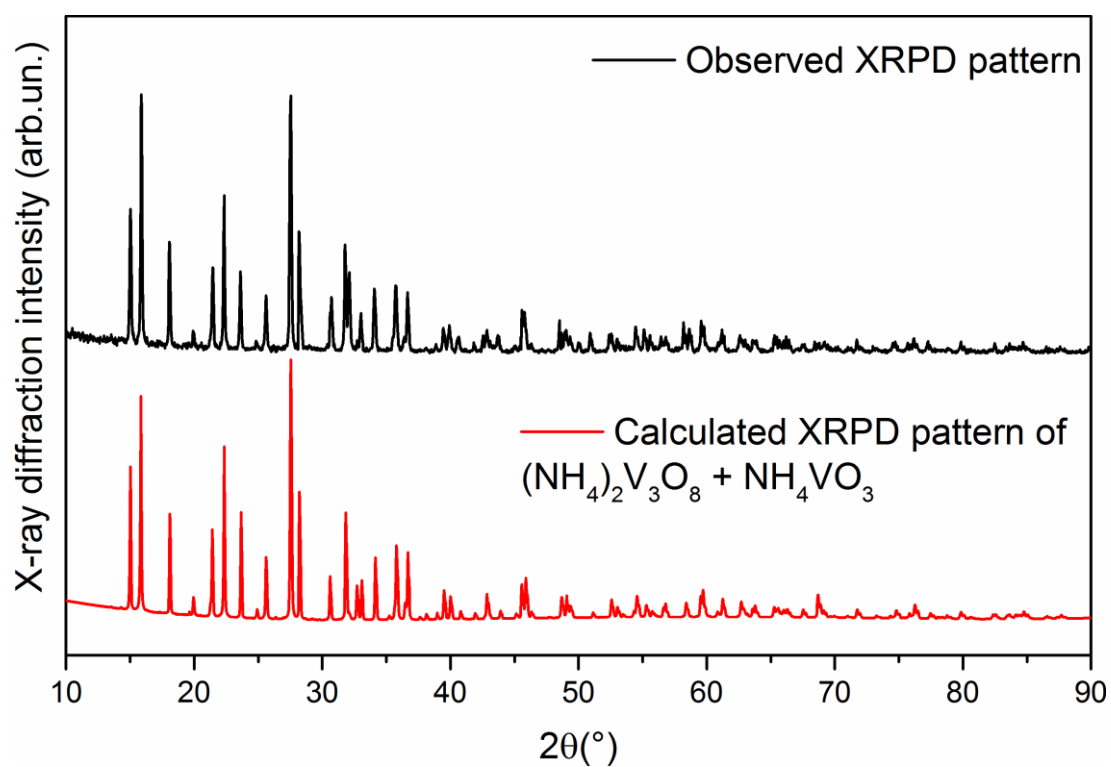
Determination of pH as a function of the NH₃/V molar ratio

A suspension of NH_4VO_3 (229 mg, 1.96 mmol) in H_2O (ca. 20 mL) was stirred at 70°C until a clear yellow solution was obtained ($[V] \approx 0.1$ mol/L). Once cooled to room temperature, stepwise addition of NH_3 (1.18 mol/L in H_2O) was performed and pH values as a function of the NH_3/V molar ratio were determined (see Figure S2).

Some relevant values are: NH_3/V = 0, pH = 7.0; NH_3/V = 0.1, pH = 8.4; NH_3/V = 1.0, pH = 9.4; NH_3/V = 2.1, pH = 9.7; NH_3/V > 4, pH = 10.0-10.3.

Figure S2. Plot of pH as a function of NH_3/V molar ratio determined with titration of solution 0.1 mol/L in vanadium (from NH_4VO_3) with 1.18 mol/L NH_3. Enlarged view of the 0-3.5 molar ratio region is given below.
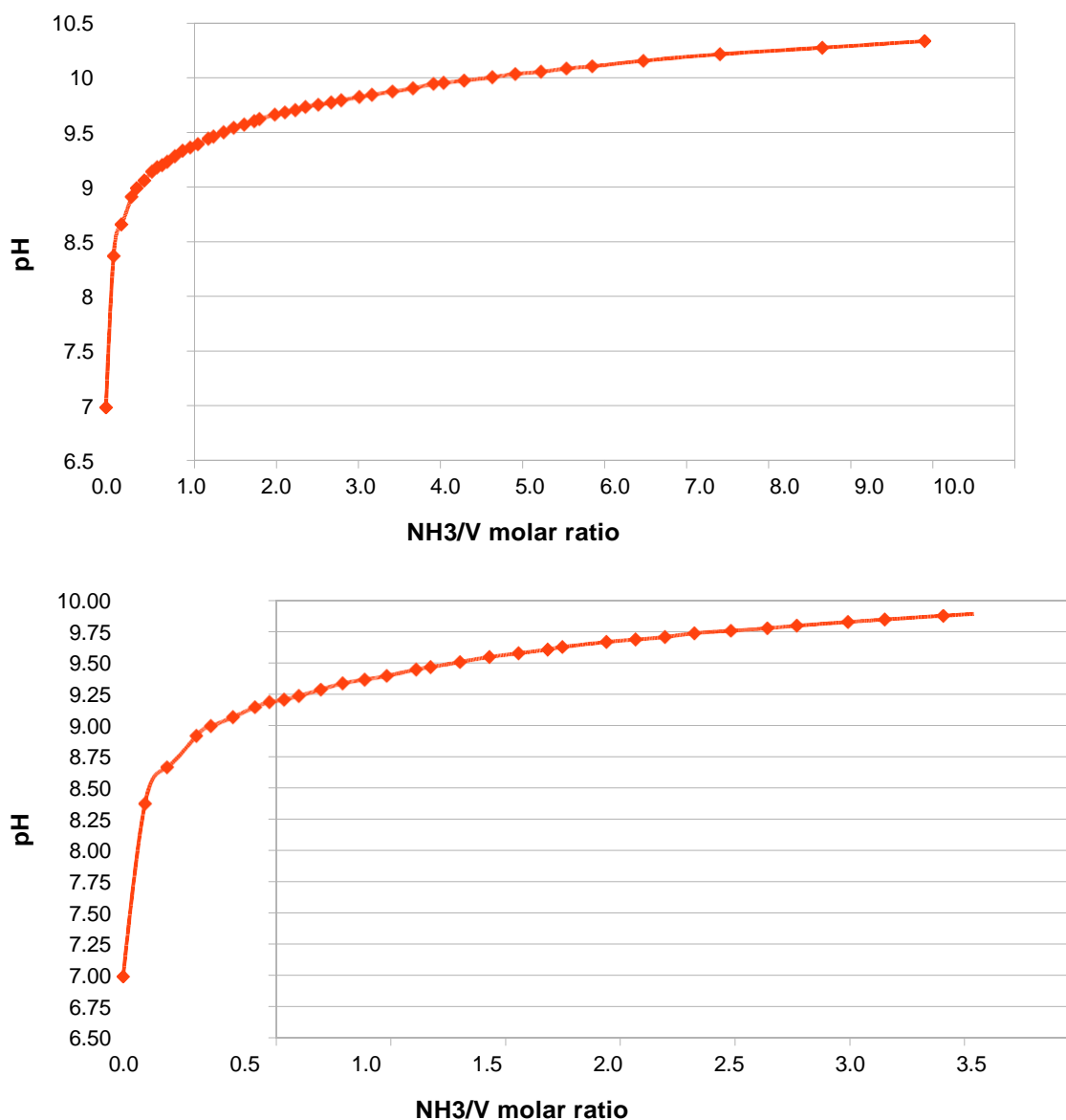
Table S2. Experimental optimization of L-pyrroline-2-carboxylate (P2C⁻) yield from the reaction of NH_4VO_3 with L-Proline.

Exp.	V concentration[a]	NH₃/V molar ratio (pH[a])	V/L-Proline molar ratio	Temp.	Reac. Time	P2C⁻ NMR yield	Notes
#1	0.84 mol/L	0.1 (8.4)	4.0	70°C	55 h	0	No reaction, only L-Proline in solution
#2	0.84 mol/L	1.0 (9.4)	4.0	70°C	45 h	40%	
#3	0.84 mol/L	2.1 (9.7)	4.0	70°C	42 h 65 h	20% 25%	
#4	0.84 mol/L	12.2 with NaOH	4.0	70°C	55 h	0	No reaction, only L-Proline in solution
#5	0.84 mol/L	14.3 with NaOH	4.0	70°C	55 h	0	No reaction, only L-Proline in solution
#6	1.6 mol/L	1.0 (9.4)	1.0	70°C	18 h	10%	
#7	1.6 mol/L	1.0 (9.4)	2.0	70°C	19 h 40 h	30% 30%	
#8	1.6 mol/L	1.0 (9.4)	4.0	70°C	12 h 31h	35% 60%	
#9	1.6 mol/L	1.0 (9.4)	8.0	70°C	18 h 42 h	30% 50%	
#10	0.6 mol/L	1.0 (9.4)	4.0	70°C	25 h 45 h	40% 50%	
#11	1.0 mol/L	1.0 (9.4)	4.0	70°C	17 h 25 h	45% 55%	
#12	1.6 mol/L	1.0 (9.4)	4.0	70°C	12 h 31 h	35% 60%	
#13	2.0 mol/L	1.0 (9.4)	4.0	70°C	17 h 25 h	40% 50%	
#14	1.0 mol/L	1.0 (9.4)	4.0	70°C	1 h 17 h 25 h 46 h 67 h	0 45% 55% ≈ 60% < 40%	Byproducts were detected after 67 h.
#15	1.0 mol/L	1.0 (9.4)	4.0	100°C	20.5 h 44 h	0	Only L-Proline in solution, but reaction mixture darkened

[a] Vanadium concentration and pH are only formal values as we are dealing with suspensions. The NH₃/V titration curve for the evaluation of pH has been obtained at a lower V concentration (0.1 mol/L) when all the vanadate precursor was dissolved (see pag. S4).

Analysis of vanadate species in the reaction mixture by ^{51}V NMR spectroscopy

The predominant V(V) species within the pH interval 9-10 for concentrated solutions ([V] > 0.1 mol/L) are $[HVO_4]^-$, $[HV_2O_7]^{3-}$ and higher-nuclearity oxoanions (tetra- and penta-vanadate species).[2,5] As a matter of fact, a solution prepared with equimolar amounts of NH_3 and NH_4VO_3 ([V] = 0.1 M, pH = 9.4) showed four ^{51}V NMR resonances (Figure S3):

i) −539 ppm, typical of $[HVO_4]^-$.[6,7]

ii) −565 ppm, typical of $[HV_2O_7]^{3-}$.[7,8]

iii) −576 ppm. ^{51}V NMR signals within the range −574 to −578 ppm have been assigned to the cyclic tetravanadate ion $[V_4O_{12}]^{4-}$ [7,9,10] or alternatively to linear V_4 species as $[HV_4O_{13}]^{5-}$ or $[V_4O_{13}]^{6-}$.[5,6,8]

iv) −584 ppm. ^{51}V NMR signals around −585 ppm have been assigned to the cyclic pentavanadate ion $[V_5O_{15}]^{5-}$ [7,8,11]

Figure S3. ^{51}V NMR spectrum of a pH = 9.4 solution prepared with NH_4VO_3 ([V] = 0.1 M) and NH_3 (NH_3/V molar ratio = 1.0).
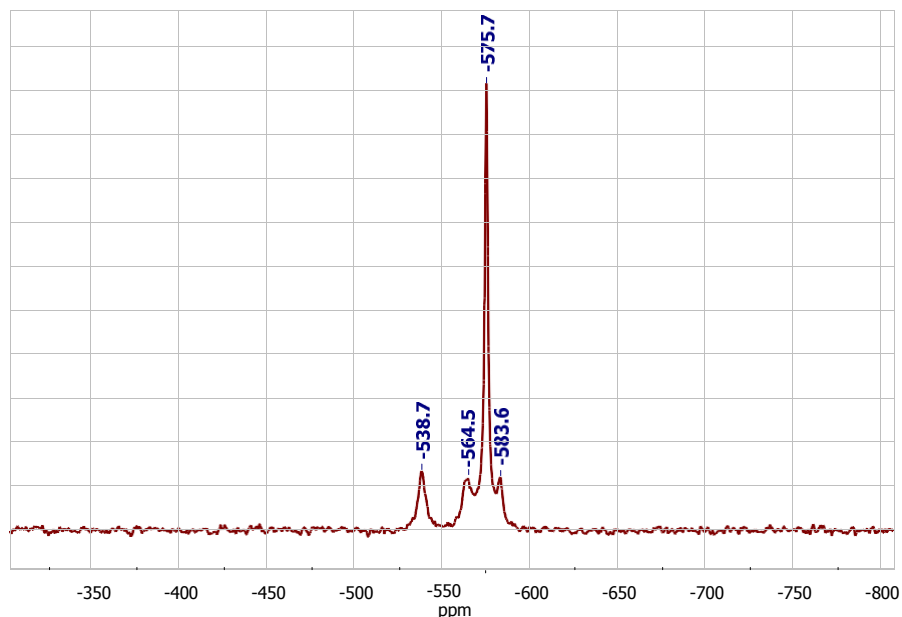
[5] N. McCann, M. Wagner, H. Hasse, *Dalton Trans.*, 2013, **42**, 2622-2628.
[6] E. Heath, O. W. Howarth, *J. Chem. Soc., Dalton Trans.*, 1981, 1105-1110.
[7] D. Rehder, M. Casny, R. Grosse, *Magn. Reson. Chem.* 2004; **42**: 745–749.
[8] D. C. Crans, A. S. Tracey, *The Chemistry of Vanadium in Aqueous and Nonaqueous Solution*, ACS Symposium Series, 1998, 711.
[9] S. E. O'Donnell, M. T. Pope, *J. Chem. Soc., Dalton Trans.*, 1976, 2290-2297.
[10] M. A. Habayeb, O. E. Hileman Jr., *Can. J. Chem.*, **58**, 1980, 2255-2261.
[11] A. M. Amado, M. Aureliano, P. J. A. Ribeiro-Claro, J. J. Teixeira-Dias, *J. Raman Spectros.*, 1993, **24**, 699-703.

During [51]V NMR monitoring of the NH$_4$VO$_3$/L-Proline/NH$_3$ reaction system (see Experimental), we observed three signals, corresponding to [HVO$_4$]$^-$, [HV$_2$O$_7$]$^{3-}$ and tetravanadate (Table S3 and Figure S4). The signal due to tetravanadate species was absent at the beginning of the reaction (yellow line in Fig. S2) while becoming the major species during the course of the reaction.

Table S3 and Figure S4. Overlay of [51]V spectra at selected time intervals of the NH$_4$VO$_3$/L-Proline/NH$_3$ reaction system and corresponding pH and ^{13}C NMR yield of pyrroline-2-carboxylate.

Reaction time	pH	P2C yield (^{13}C NMR)[a]	[51]V NMR Line colour
1 h	9.8	0 %	Yellow
21.5 h	9.9	≈ 45 %	green
24 h			cyan
26.5 h	9.5	≈ 55 %	blue
33.5 h			violet
48 h	9.6	≈ 60%	red

[a] Yields taken from Entry #14 in Table S2 at comparable reaction times.
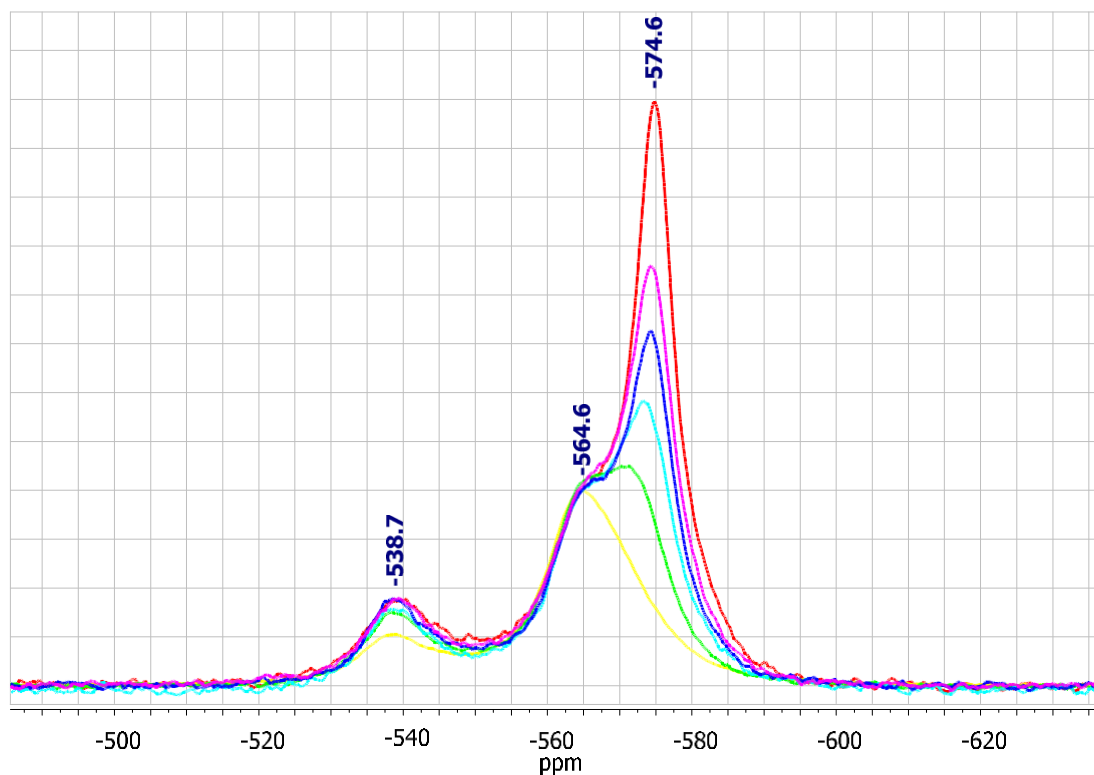
Calculation of a plausible reduction potential for the V(V)/V(IV) couple under the experimental conditions used in the reactions

It is difficult to provide a meaningful reduction potential for the V(V)/V(IV) couple under conditions relevant to the oxidation of L-Proline, since V(V) species with different nuclearity and protonation state are present in solution (see Pag S7) and can be involved in the redox reaction. The reaction mechanism proposed by DFT calculations considered the transformation of the V(V) cyclic tetravanadate $[H_2V_4O_{12}]^{2-}$ to the mixed valence V(V)/V(IV) compound $[H_4V_4O_{12}]^{2-}$ of the same nuclearity. On the other hand, thermodynamic data available in the literature for tetranuclear V(V) and V(IV) species, compiled in Table S4, are related to $[V_4O_{12}]^{4-}$ and $[V_4O_9]^{2-}$. These ions are the conjugate base of $[H_2V_4O_{12}]^{2-}$ and the fully reduced (and deprotonated) counterpart of $[H_4V_4O_{12}]^{2-}$, respectively, which have been used in DFT calculations.

Table S4. Thermodynamic data on $[V_4O_{12}]^{4-}_{(aq)}$ and $[V_4O_9]^{2-}_{(aq)}$ ions in aqueous solution.

	Reaction	$\Delta G°$ (298 K)	Ref.
Eq. (S8)	$[VO_4]^{3-}_{(aq)} + 2\ H^+_{(aq)} \rightarrow [H_2VO_4]^-_{(aq)}$	− 122 kJ/mol	[1]
Eq. (S9)	$4\ [H_2VO_4]^-_{(aq)} \rightarrow [V_4O_{12}]^{4-}_{(aq)} + 4\ H_2O$	− 80 kJ/mol	[5]
Eq. (S10)	$4\ [VO_4]^{3-}_{(aq)} + 14\ H^+_{(aq)} + 4\ e^- \rightarrow [V_4O_9]^{2-}_{(aq)} + 7\ H_2O$	− 846 kJ/mol	[1]

Using these data, a standard reduction potential of $E° = + 0.72$ V (corresponding to $\Delta G° = −278$ kJ/mol) can be calculated for the $V_4(V) \rightarrow V_4(IV)$ transformation reported in Eq. (S11) at 298 K.

$$(S11) \qquad [V_4O_{12}]^{4-}_{(aq)} + 6\ H^+_{(aq)} + 4\ e^- \rightarrow [V_4O_9]^{2-}_{(aq)} + 3\ H_2O$$
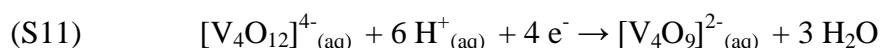
Therefore, on considering the variation of the potential with pH as $E°' = E° - 6 \cdot \frac{RT}{nF\log e} \cdot pH$, values of $E°'$ at different pH were calculated:

For pH = 14, $E°' = −0.52$ V, corresponding to the standard reduction potential for Eq. (S12).

$$(S12) \qquad [V_4O_{12}]^{4-}_{(aq)} + 4\ e^- \rightarrow [V_4O_9]^{2-}_{(aq)} + 6\ OH^-_{(aq)}$$
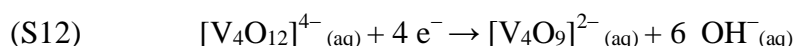
For pH = 10 $E°' = −0.17$ V

For pH = 9 $E°' = −0.08$ V

Figure S5. DFT-optimized structure of intermediates **C** and **C-is2** and Gibbs energy difference (kcal mol^{-1}, T = 343.15 K). C-PCM/ωB97X calculations, water as continuous medium. Colour map: light grey, hydrogen; dark grey, carbon; red, oxygen; blue, nitrogen; green, vanadium; light blue, spin density surface (isovalue = 0.01 a.u.).
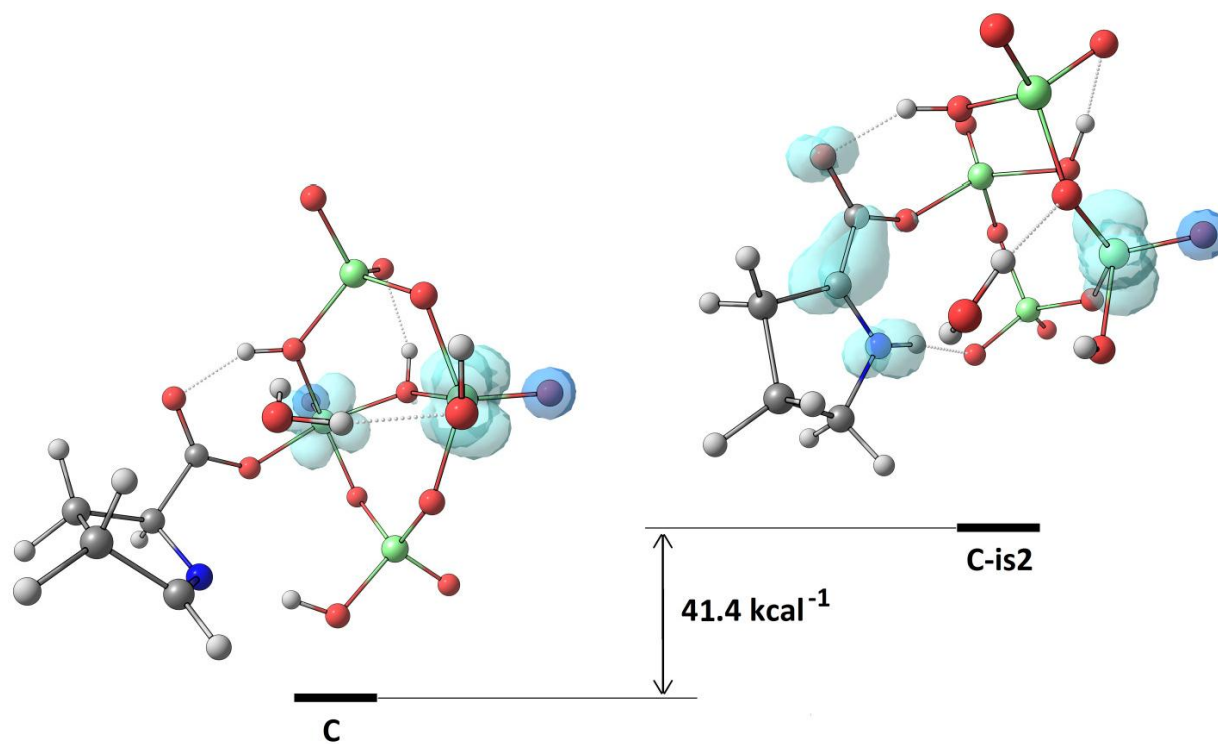

41.4 kcal^{-1}

C-is2

C

Figure S6. DFT-optimized structure of $[V_4O_{10}(OH)_2(sarcosinate)\cdot H_2O]^{3-}$. C-PCM/ωB97X calculations, water as continuous medium. Colour map: light grey, hydrogen; dark grey, carbon; red, oxygen; blue, nitrogen; green, vanadium. Selected computed bond lengths: V−$O_{carboxylate}$ 2.057 Å, $O_{carboxylate}$---H, 1.558 Å, O−H(---$O_{carboxylate}$) 1.008 Å. Cartesian coordinates are collected in a separated. xyz file.

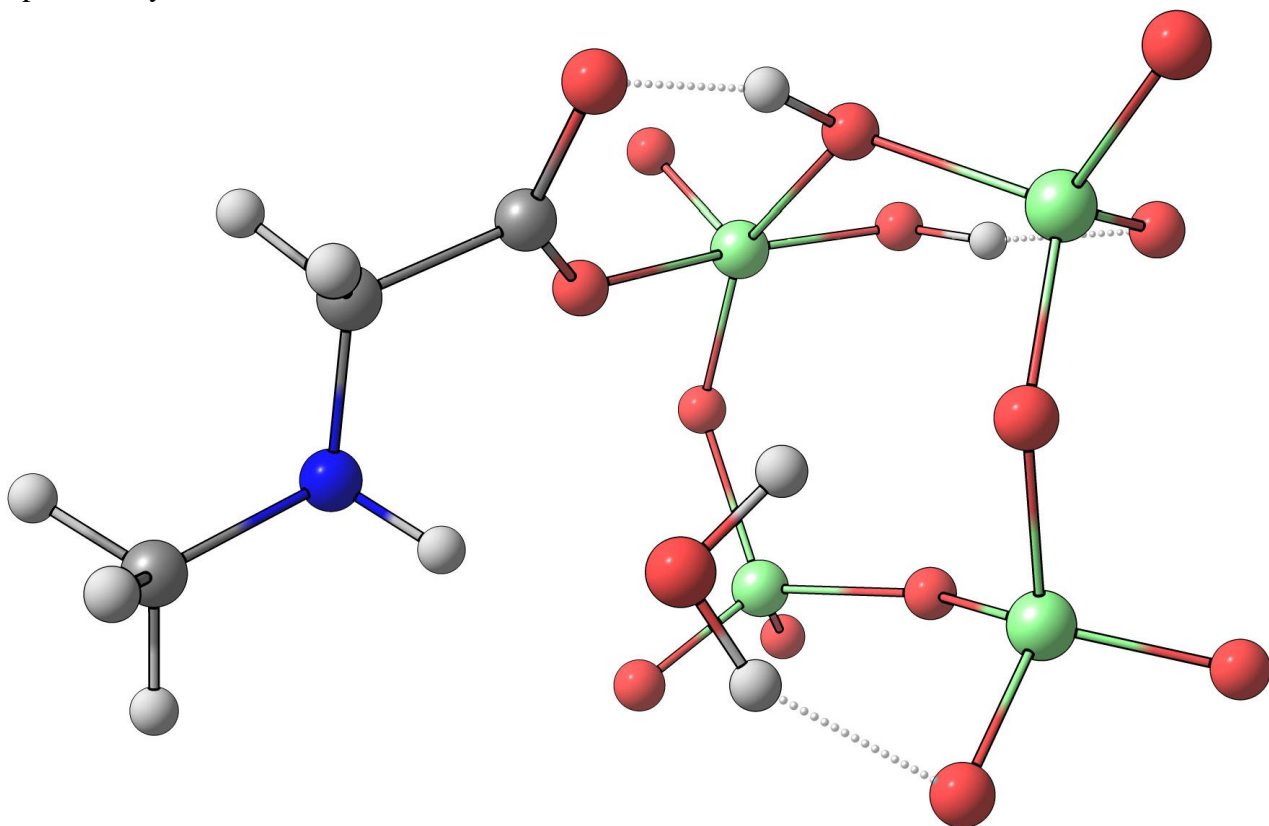**Figure S7**. Relative Gibbs energy values (kcal mol^{-1}, T = 298.15 K) of possible intermediates involved in the oxidation of L-prolinate to pirrolidine-2-carboxylate. C-PCM/ωB97X calculations, water as continuous medium. Black line: isotope ^{1}H for all hydrogen atoms. Blue line: isotope ^{2}H for the N- and O-bonded hydrogen atoms.