

Supporting information

Hydrolysis of carboxyesters promoted by vanadium (V) oxyanions

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Figure 1S: ^{51}V NMR spectrum of 25mM Na_3VO_4 at pH = 7 (MOPs buffer), solvent AcCN:H₂O=1:9. Dimeric V2, tetrameric V4 and pentameric V5 polyoxoanions, evidenced by their characteristic 51V NMR signals at -567.71, -572.89 ppm and -580.91 ppm respectively

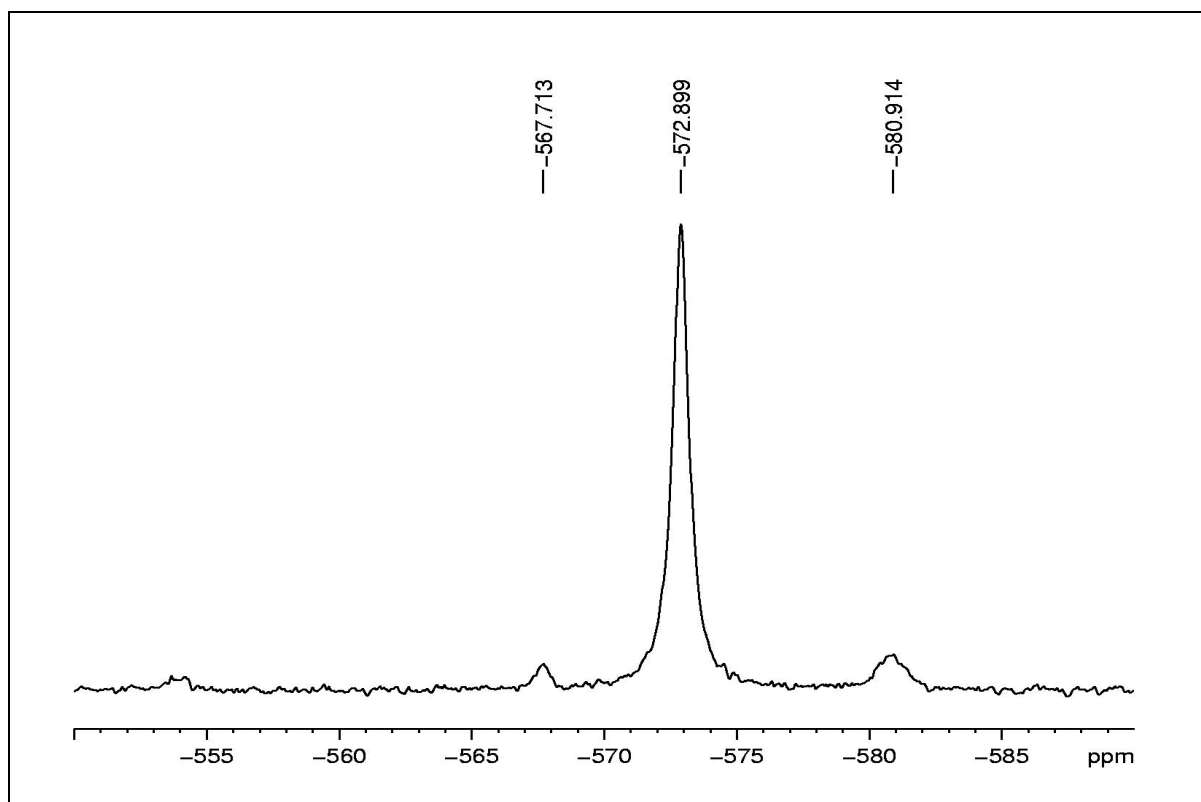


Figure 2S: Full ^1H NMR spectra of the reaction between 5mM pNPA and 25mM Na_3VO_4 at $\text{pD} = 7.4$ and 37°C in $\text{AcCN}:\text{D}_2\text{O}$ (10: 90) solvent mixture, measured at different time increments. Disappearance of the methyl peak of pNPA at 2.46 ppm and appearance of acetate peak at 1.81ppm could be observed in the course of hydrolytic reaction.

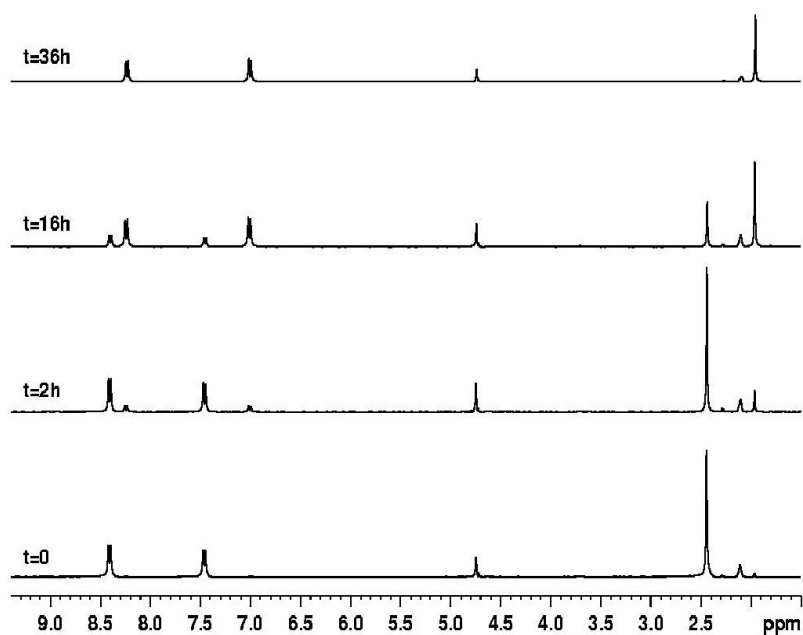


Figure 3S. EPR spectra of the following samples:

A: 25 mM VOSO_4 in water. This sample was used as a reference since in this sample V is in +4 oxidation state and therefore EPR active.

B: 0.25 mM VOSO_4 in water

C: Na_3VO_4 25 mM, Mops 100mM, pH 7.0, D_2O : CD_3CN = 90/10. In this sample vanadium is in + 5 oxidation state and therefore it is EPR silent.

D: Na_3VO_4 25 mM, Mops 100mM, pH 7.0, pNPA 5mM, measured after mixing, D_2O : CD_3CN = 90/10

E: Na_3VO_4 25 mM, Mops 100mM, pH 7.0, pNPA 5mM, measured after 5 hours of reaction, D_2O : CD_3CN = 90/10. The same spectrum was obtained after 30 hours of reaction.

F: sample E to which 3 drops Acetylacetonate + metallic Zn grain (as reducing agent) was added and let to reacted for 5 min at room temperature. The appearance of the EPR signal indicates that V(V) was reduced to V(IV) upon addition of reducing agent.

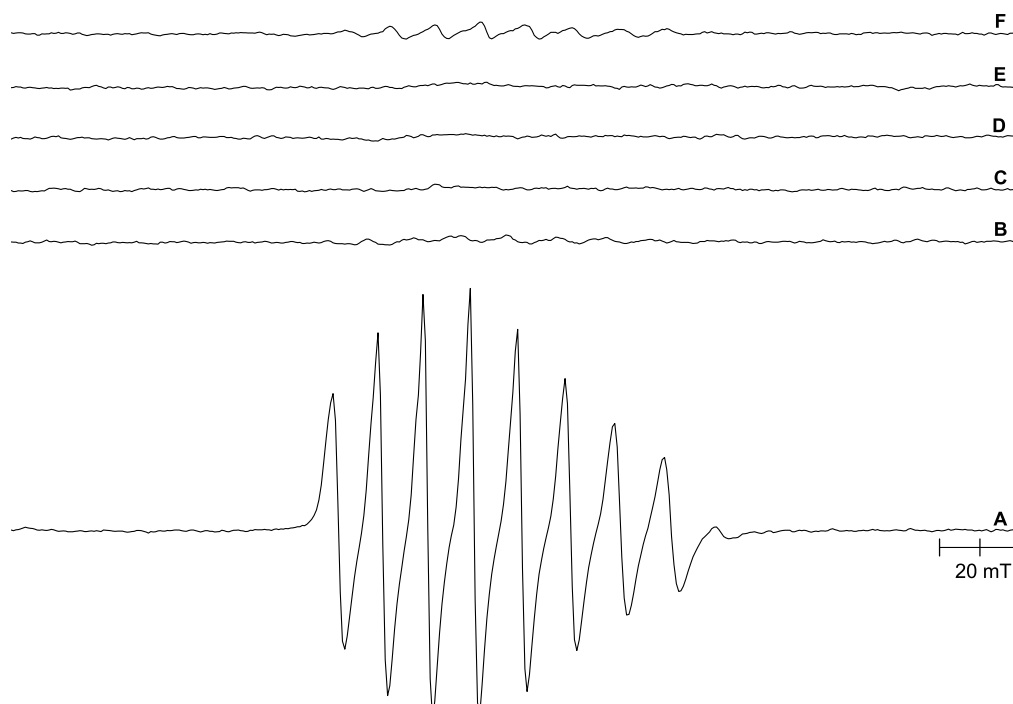


Figure 4S. ^{51}V NMR spectra of a solution containing 1mM Na_3VO_4 recorded in the absence and the presence of 20mM pNPA at pH 7.0 and 37°C.

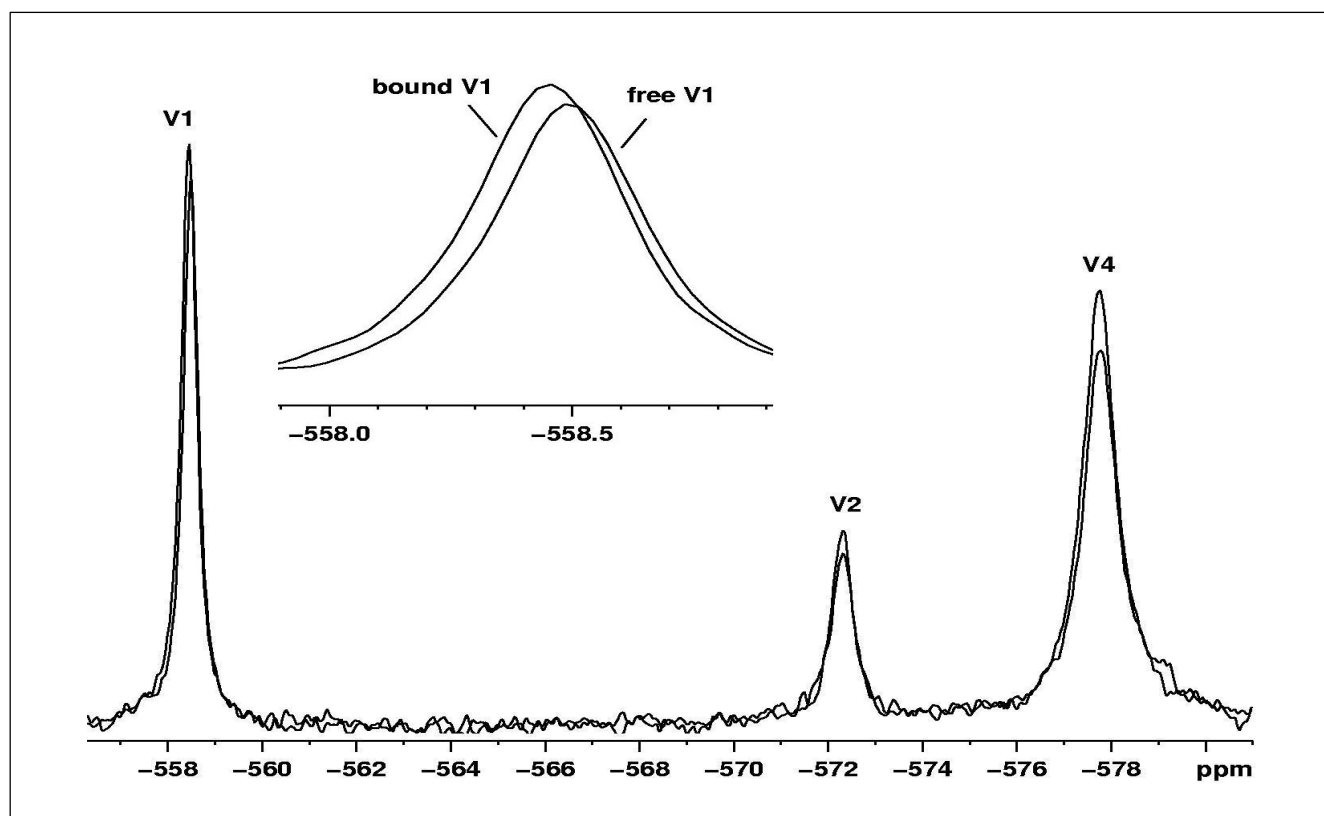


Figure 5S: Influence of the concentration of NaClO₄ on the rate constant k_{obs} of reaction between VO₄³⁻ 25mM + pNPA5mM, pD=7.1 (MOPs), AcCN/D₂O= 10/90

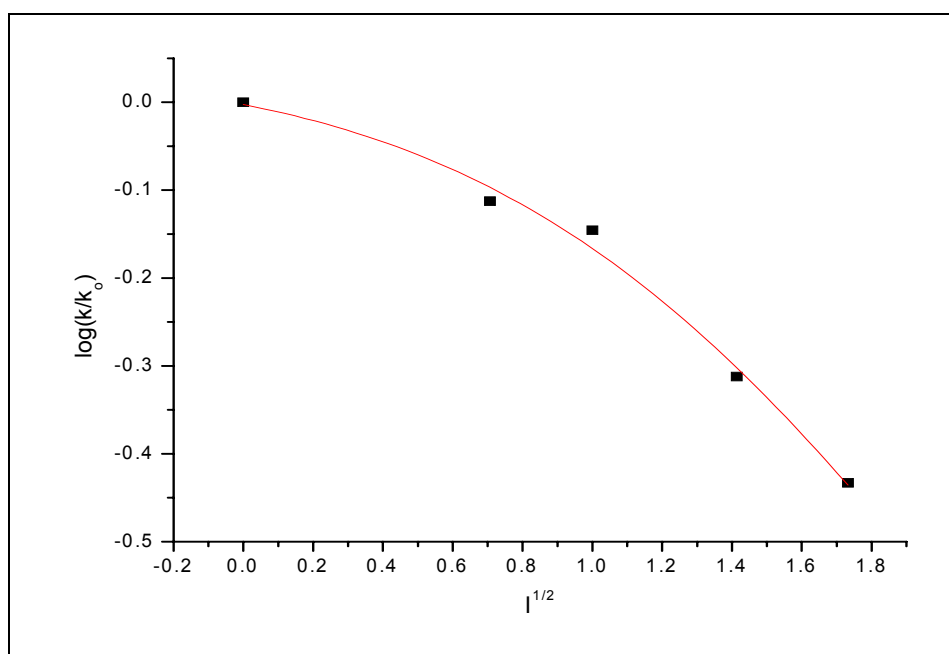
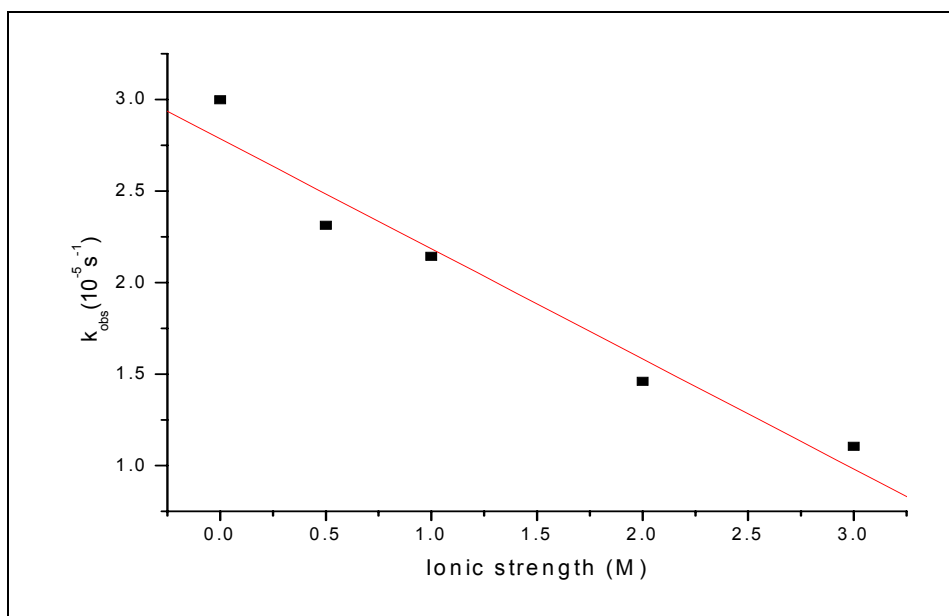


Figure 6S: a-Arrhenius plot of $\ln(k_{\text{obs}})$ as a function of $1/T$ and b-Eyring plot

$\ln(k_{\text{obs}}/T)$ as a function of $1/T$.

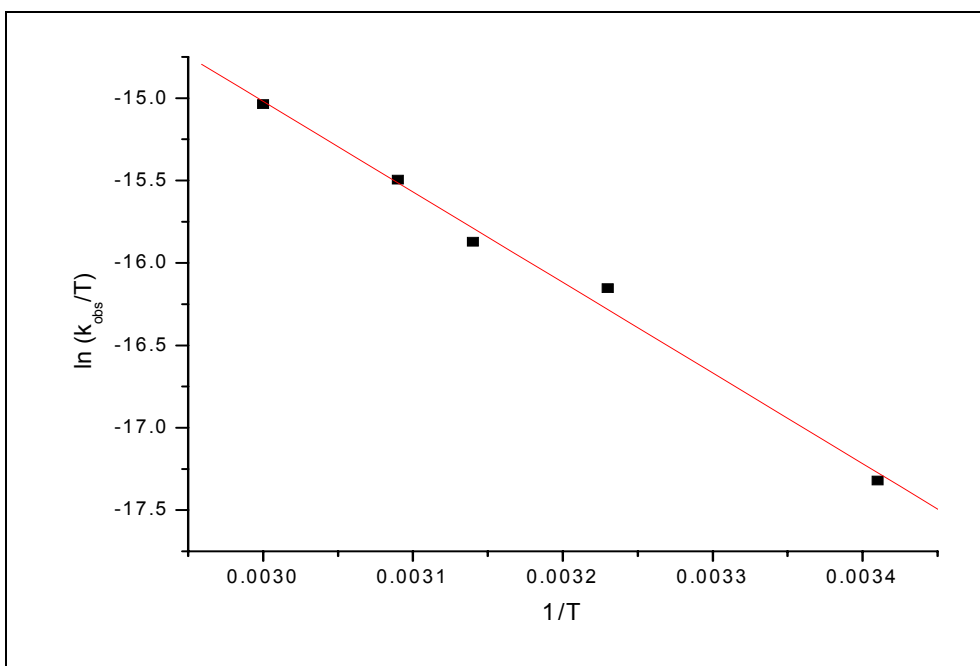
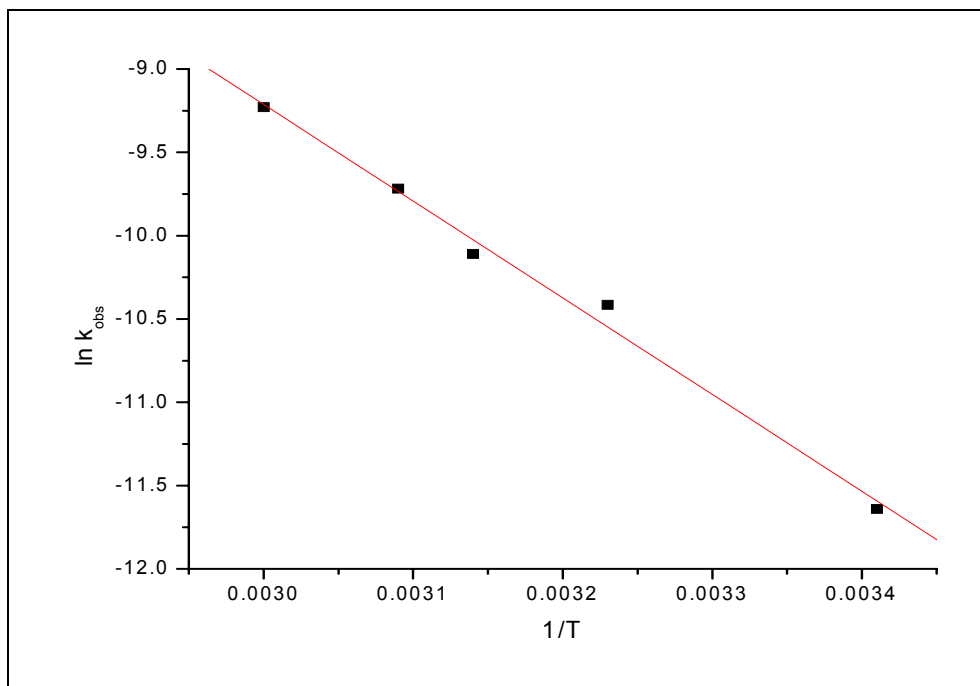


Table S1: Influence of pH on k_{obs} of reaction between pNPA and VO_4^{3-} , $T = 310\text{K}$, solvent AcCN:D₂O = 10/90, MOPs buffer pD = 5-10.

pH	$k_{\text{obs}} \text{ (s}^{-1}\text{)}$		
	pNPA	pNPA+V ₁	Δ
5.0	$1.011 \cdot 10^{-6}$	$1.283 \cdot 10^{-6}$	$2.72 \cdot 10^{-7}$
6.0	$1.158 \cdot 10^{-6}$	$1.017 \cdot 10^{-5}$	$9.012 \cdot 10^{-6}$
7.1	$2.600 \cdot 10^{-6}$	$2.998 \cdot 10^{-5}$	$2.738 \cdot 10^{-5}$
7.5	$5.714 \cdot 10^{-6}$	$5.005 \cdot 10^{-5}$	$4.434 \cdot 10^{-5}$
8.1	$1.279 \cdot 10^{-5}$	$6.965 \cdot 10^{-5}$	$5.686 \cdot 10^{-5}$
9.0	$1.654 \cdot 10^{-4}$	$2.495 \cdot 10^{-4}$	$8.410 \cdot 10^{-5}$
10.0	$8.121 \cdot 10^{-4}$	$1.371 \cdot 10^{-3}$	$5.589 \cdot 10^{-4}$