Electronic Supporting Information File

Surface Ligand Length Influences Kinetics of H-atom Uptake in Polyoxovanadate-alkoxide Clusters

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Figure S1. ¹H NMR spectrum [n Oct₄N][V₆O₇(OCH₃)₁₂] in CD₃CN at 21 °C.



Figure S2. Electronic absorption spectrum of [ⁿOct₄N][V₆O₇(OCH₃)₁₂] in THF 21 °C.



Figure S3. ESI-MS(-ve) of 1-butyl, $[^{n}Bu_{4}N][V_{6}O_{7}(OC_{4}H_{9})_{12-x}(OCH_{3})_{x}]$ (x = 0, 1, 2, 3, 4).



Figure S4. Electronic absorption spectra of 2-methyl, 2-ethyl, 2-propyl and 2-butyl in acetonitrile at 21 °C



Figure S5. ¹H NMR spectra of equilibrium reaction solutions with **1-methyl** and Hydz after 6 hours in THF- d_8 at 21 °C.

Table S1.	BDFE(O-H) _{adj} calculated from equilibrium reactions of 1-methyl with Hydz after 6
	hours using the equation outlined in the Experimental section.

			Hydz								
	7.16 ppm (4 H) 6.77 ppm (6 H)		7.16 ppm (4 H) 6.77 ppm (6 H)			7.91 pp	opm (4 H) 7.58 ppm (6 H)			Ava	
		Relative		Relative	Avg.		Relative		Relative	Avg.	BDFE _{adj}
Trial	Integral	Conc. ^a	Integral	Conc. ^a	Conc.	Integral	Conc. ^a	Integral	Conc. ^a	Conc.	(kcal/mol)
Α	0.33	0.08	0.40	0.07	0.08	0.06	0.02	0.10	0.02	0.02	59.9
В	0.35	0.09	0.38	0.06	0.08	0.06	0.02	0.09	0.02	0.02	59.9
С	0.34	0.09	0.41	0.07	0.08	0.06	0.02	0.09	0.02	0.02	59.9
^{<i>a</i>} Relative concentration of either Hydz or azobenzene was determined by dividing the integral by the number of protons a Avg.										59.9	
given s	signal(s) corre	esponds with.	-		-	C				Error	0.1

given signal(s) corresponds with. ^b Integration of the N-H resonance of Hydz was omitted in this study due to potential broadening of the resonance by Hbonding with **2-V₆O₈²⁻**.



Figure S6. ¹H NMR spectra of equilibrium reaction solutions with **1-ethyl** and Hydz after 7 days in THF- d_8 at 21 °C.

Table S2. BDFE(O-H)_{adj} calculated from equilibrium reactions of **1-ethyl** with Hydz after 7 days using the equation outlined in the Experimental section.

			Hydz								
	7.16 ppm (4 H) 6.77 ppm (6 H)		7.16 ppm (4 H) 6.77 ppm (6 H)		Aug	7.91 pp	m (4 H)	7.58 рр	m (6 H)	Ava	
		Relative		Relative	Avg. Conc		Relative		Relative	Avg.	$\mathbf{BDFE}_{\mathrm{adj}}$
Trial	Integral	Conc. ^a	Integral	Conc. ^a	Conc.	Integral	Conc. ^a	Integral	Conc. ^a	Conc.	(kcal/mol)
Α	0.40	0.10	0.59	0.01	0.09	0.05	0.01	0.06	0.01	0.01	59.8
В	0.41	0.10	0.60	0.10	0.10	0.03	0.01	0.06	0.01	0.01	59.7
C	0.56	0.14	0.83	0.14	0.14	0.06	0.02	0.06	0.02	0.01	59.7
^a Relative concentration of either Hydz or azobenzene was determined by dividing the integral by the number of protons a Avg.											59.7
given s	ignal(s) corre	sponds with.	, u 200 0 1					// 01 p1		Error	0.1

^b Integration of the N-H resonance of Hydz was omitted in this study due to potential broadening of the resonance by Hbonding with **2-V₆O₈²⁻**.



Figure S7. ¹H NMR spectra of equilibrium reaction solutions with 1-propyl and Hydz after 7 days in THF-*d*₈ at 21 °C.

Table S3. BDFE(O-H)adj calculated from equilibrium reactions of 1-propyl with Hydz after 7 days using the equation outlined in the Experimental section.

			Hydz								
	7.16 ppm (4 H) 6.77 ppm (6 H)			A	7.91 pp	om (4 H)	7.58 pp	m (6 H)	A - 1/2		
		Relative		Relative	Avg.		Relative		Relative	Avg. Conc	BDFEadj
Trial	Integral	Conc. ^a	Integral	Conc. ^a	Conc.	Integral	Conc. ^a	Integral	Conc. ^a	Conc.	(kcal/mol)
A	0.28	0.07	0.43	0.07	0.07	0.03	0.01	0.04	0.01	0.01	59.7
В	0.41	0.10	0.60	0.10	0.10	0.03	0.01	0.05	0.01	0.01	59.6
C	0.39	0.10	0.55	0.09	0.09	0.04	0.01	0.06	0.01	0.01	59.7
	a concentrativ	on of either H	udz or azaber	nzene was det	armined by	dividing the	integral by the	a number of r	urotons a	Avg.	59.7

Error

0.1

Relative concentration of either Hydz or azobenzene was determined by dividing the integral by the number of protons a given signal(s) corresponds with. ^b Integration of the N-H resonance of Hydz was omitted in this study due to potential broadening of the resonance by H-

bonding with 2-V6O82-.



Figure S8. ¹H NMR spectra of equilibrium reaction solutions with **1-butyl** and Hydz after 7 days in THF- d_8 at 21 °C.

 Table S4.
 BDFE(O-H)_{adj} calculated from equilibrium reactions of 1-butyl with Hydz after 7 days using the equation outlined in the Experimental section

			Hydz								
	7.16 ppm (4 H) 6.77 ppm (6 H)		7.16 ppm (4 H) 6.77 ppm (6 H) 7.91 ppm (4 H) 7.58 ppm (6 H				m (6 H)	A			
		Relative		Relative	Avg.		Relative		Relative	Avg. Cono	BDFE _{adj}
Trial	Integral	Conc. ^a	Integral	Conc. ^a	Conc.	Integral	Conc. ^a	Integral	Conc. ^a	Conc.	(kcal/mol)
А	0.34	0.09	0.60	0.10	0.09	0.05	0.01	0.08	0.01	0.01	59.8
В	0.32	0.08	0.64	0.11	0.09	0.04	0.01	0.05	0.01	0.01	59.8
С	0.37	0.09	0.62	0.10	0.10	0.06	0.02	0.08	0.01	0.01	59.8
Avg.										59.8	
given	signal(s) cor	responds with	iyuz of azob	enzene was de		y arviding th	e megral by t	ne number of	protons a	Error	0.1

^b Integration of the N-H resonance of Hydz was omitted in this study due to potential broadening of the resonance by H-bonding with $2-V_6O_8^{2^2}$.



Figure S9. Scanning Kinetics for the reaction between **1-methyl** (0.6 mM) and H₂Phen (8 mM) recorded in acetonitrile at 25 °C. Red is initial spectrum of **1-methyl** ($t_0 = 0$ min), color of trace darkens as reaction progresses ending in the black trace ($t_f = 120$ min).



Figure S10. Plots of absorbance at 1025 nm vs. time for the reaction between **1-methyl** (0.6 mM) and excess H₂Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C.



Figure S11. Scanning Kinetics for the reaction between **1-ethyl** (0.6 mM) and H₂Phen (8 mM) recorded in acetonitrile at 25 °C. Green is initial spectrum of **1-ethyl** ($t_0 = 0$ min), color of trace darkens as reaction progresses ending in the black trace ($t_f = 120$ min).



Figure S12. Plots of absorbance at 1025 nm vs. time for the reaction between **1-ethyl** (0.6 mM) and excess H_2 Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C.



Figure S13. Scanning Kinetics for the reaction between **1-propyl** (0.6 mM) and H₂Phen (8 mM) recorded in acetonitrile at 25 °C. Dark blue is initial spectrum of **1-propyl** ($t_0 = 0$ min), color of trace darkens as reaction progresses ending in the black trace ($t_f = 120$ min).



Figure S14. Plots of absorbance at 1025 nm vs. time for the reaction between **1-propyl** (0.6 mM) and excess H_2 Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C



Figure S15. Scanning Kinetics for the reaction between **1-propyl** (0.6 mM) and H₂Phen (8 mM) recorded in acetonitrile at 25 °C. Dark blue is initial spectrum of **1-propyl** ($t_0 = 0$ min), color of trace darkens as reaction progresses ending in the black trace ($t_f = 120$ min).



Figure S16. Plots of absorbance at 1025 nm vs. time for the reaction between **1-butyl** (0.6 mM) and excess H_2 Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C.



Figure S17. Plots of absorbance at 1025 nm vs. time for the reaction between **1-methyl** (0.6 mM) and excess D_2 Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C.



Figure S18. Plots of absorbance at 1025 nm vs. time for the reaction between **1-ethyl** (0.6 mM) and excess D_2 Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C



Figure S19. Plots of absorbance at 1025 nm vs. time for the reaction between **1-propyl** (0.6 mM) and excess D_2 Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C.



Figure S20. Plots of absorbance at 1025 nm vs. time for the reaction between **1-butyl** (0.6 mM) and excess D_2 Phen under pseudo first-order reaction conditions recorded in acetonitrile at 25 °C.



Figure S21. Plots of absorbance at 1025 nm vs. time for the reaction between **1-methyl** (0.6 mM) and H₂Phen (8 mM) recorded in acetonitrile between 0 °C and 35 °C.



Figure S22. Plots of absorbance at 1025 nm vs. time for the reaction between **1-ethyl** (0.6 mM) and H_2 Phen (8 mM) recorded in acetonitrile between 10 °C and 45 °C.



Figure S23. Plots of absorbance at 1025 nm vs. time for the reaction between **1-propyl** (0.6 mM) and H_2 Phen (8 mM) recorded in acetonitrile between 10 °C and 45 °C.



Figure S24. Plots of absorbance at 1025 nm vs. time for the reaction between **1-butyl** (0.6 mM) and H_2 Phen (8 mM) recorded in acetonitrile between 10 °C and 45 °C.