

Kinetic studies of phosphoester hydrolysis promoted by a dimeric tetrazirconium(IV) Wells-Dawson polyoxometalate†

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Supporting information

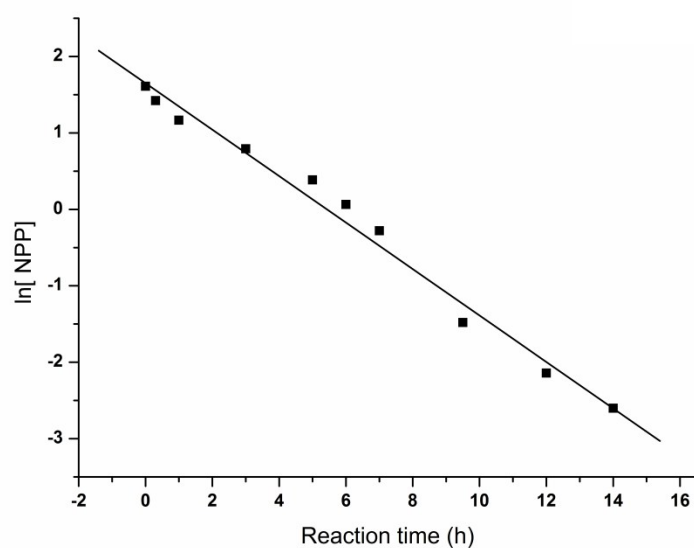


Figure S1. $\ln[\text{NPP}]$ as a function of time (linear fit with $R^2 = 0.98$) for the reaction between 5.0 mM of NPP and 1.0 mM of ZrWD 4:2 at pD 6.4 and 50 °C.

Table S1. pD dependence of the reaction rate constants for the hydrolysis of 5.0 mM of NPP in the presence of 1.0 mM of ZrWD 4:2 at 50 °C.

pD	k_{obs} in the presence of ZrWD 4:2 (10^{-5} s^{-1})	k_{obs} in the absence of ZrWD 4:2 (10^{-7} s^{-1})	Fold rate enhancement
4.4	26.6 ± 0.45	35.6 ± 0.30	75
5.4	18.4 ± 0.34	8.98 ± 0.83	205
6.4	8.44 ± 0.36	2.81 ± 0.25	300
7.4	5.16 ± 0.10	1.48 ± 0.02	349
8.4	5.13 ± 0.18	1.14 ± 0.02	450
9.4	4.02 ± 0.10	1.12 ± 0.04	376
10.4	2.54 ± 0.12	0.92 ± 0.03	276

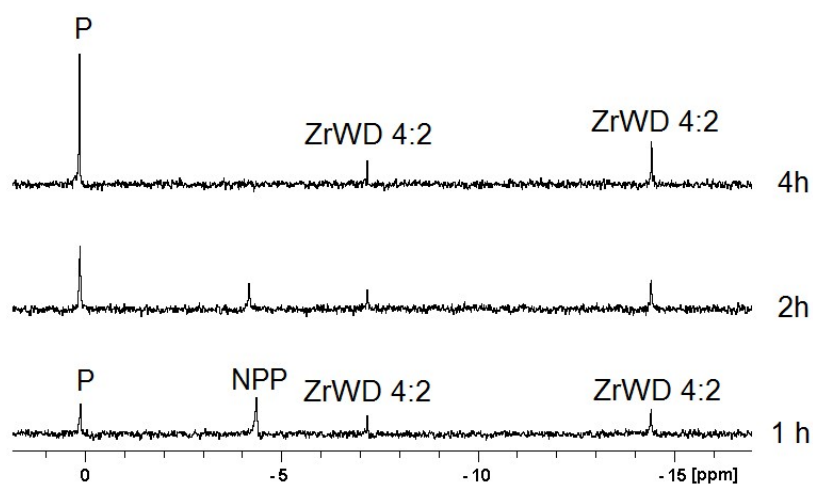


Figure S2. ^{31}P NMR spectra of the hydrolysis reaction of 5.0 mM of NPP in the presence of 1.0 mM of ZrWD 4:2 at different time intervals at pD 4.4 and 50 °C. (400 MHz, D_2O , 293 K, NS = 256, 25% H_3PO_4).

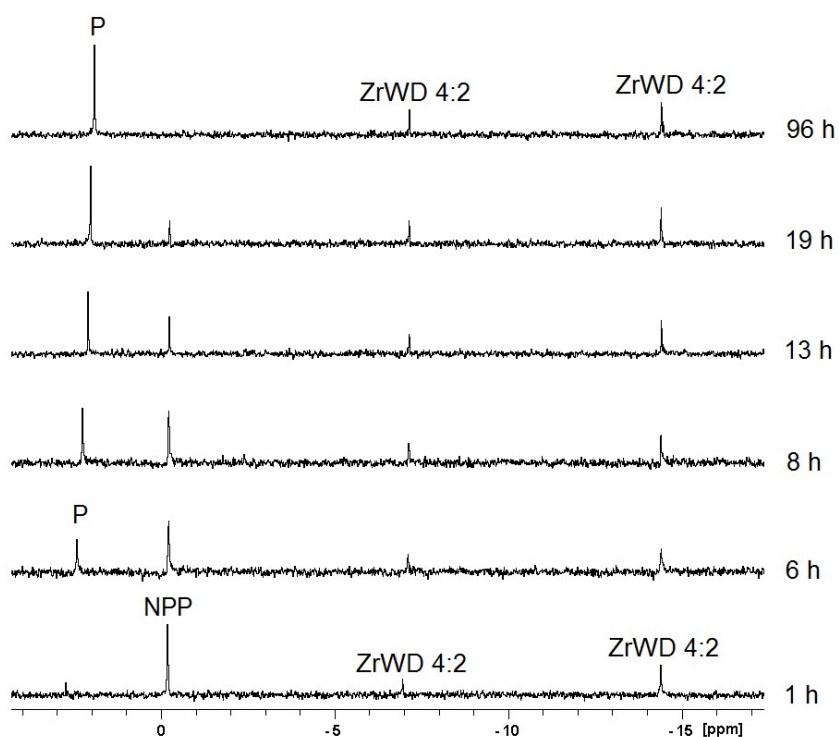


Figure S3. ^{31}P NMR spectra of the hydrolysis reaction of 5.0 mM of NPP in the presence of 1.0 mM of ZrWD 4:2 at different time intervals at pD 10.4 and 50 °C. (400 MHz, D_2O , 293 K, NS = 256, 25% H_3PO_4).

Table S2. Temperature dependence of the reaction rate constants for the hydrolysis of 5.0 mM of NPP in the presence of 1.0 mM of ZrWD 4:2 at pD 6.4 in the range of temperature from 37 °C to 80 °C.

Temperature (°C)	k_{obs} (s ⁻¹) in the presence of ZrWD 4:2	k_{obs} (s ⁻¹) in the absence of ZrWD 4:2
37	$1.63(\pm 0.40) \times 10^{-5}$	$2.35(\pm 0.65) \times 10^{-8}$
50	$8.44(\pm 0.36) \times 10^{-5}$	$2.81(\pm 0.25) \times 10^{-7}$
60	$4.22(\pm 0.60) \times 10^{-4}$	$1.10(\pm 0.30) \times 10^{-6}$
70	$1.40(\pm 0.11) \times 10^{-3}$	$4.34(\pm 0.29) \times 10^{-6}$
80	$2.59(\pm 0.34) \times 10^{-3}$	$3.61(\pm 0.70) \times 10^{-5}$

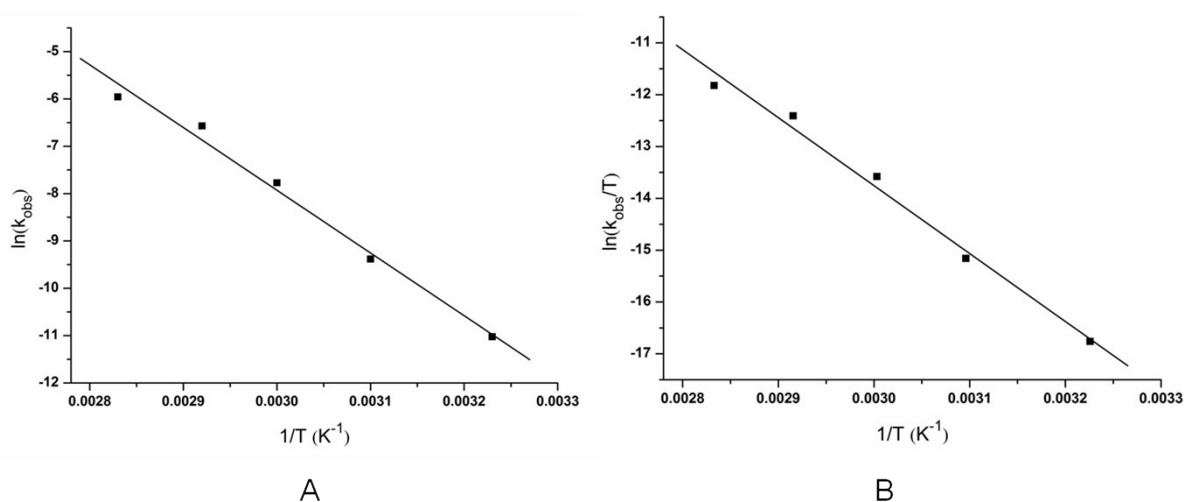


Figure S4. A: Arrhenius plot of $\ln(k_{obs})$ as a function of $1/T$ (Arrhenius equation: $\ln k_{obs} = \ln A - \frac{E_a}{R} \frac{1}{T}$) and B: Eyring plot of $\ln(k_{obs}/T)$ as a function of $1/T$ (Eyring equation: $\ln \frac{k_{obs}}{T} = -\frac{\Delta H^\ddagger}{R} \frac{1}{T} + \ln \frac{k_b}{h} + \frac{\Delta S^\ddagger}{R}$) for the hydrolysis of 5.0 mM of NPP in the presence of 1.0 mM of ZrWD 4:2 at pD 6.4 and 37 – 80 °C.

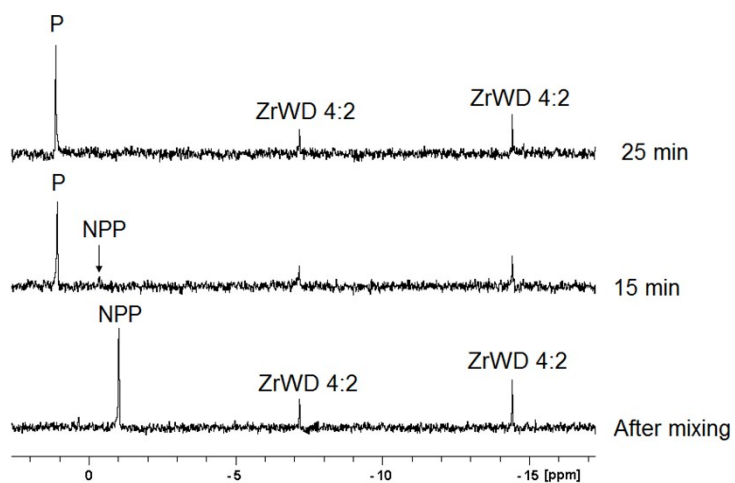


Figure S5. ^{31}P NMR spectra of the hydrolysis reaction of 5.0 mM of NPP in the presence of 1.0 mM of ZrWD 4:2 at different time intervals at pD 6.4 and 80 °C. (400 MHz, D_2O , 293 K, NS = 256, 25% H_3PO_4).

Table S3. The reaction rate constants for the hydrolysis of 5.0 mM of NPP in the presence of 0.5 – 3.0 mM ZrWD 4:2 at pD 6.4 and 50 °C.

[ZrWD 4:2] (mM)	k_{obs} (10^{-5}s^{-1})
0.5	7.92 ± 0.89
1.0	8.44 ± 0.36
1.5	13.8 ± 0.50
2.0	18.9 ± 0.90
2.5	20.1 ± 0.10
3.0	23.6 ± 0.15

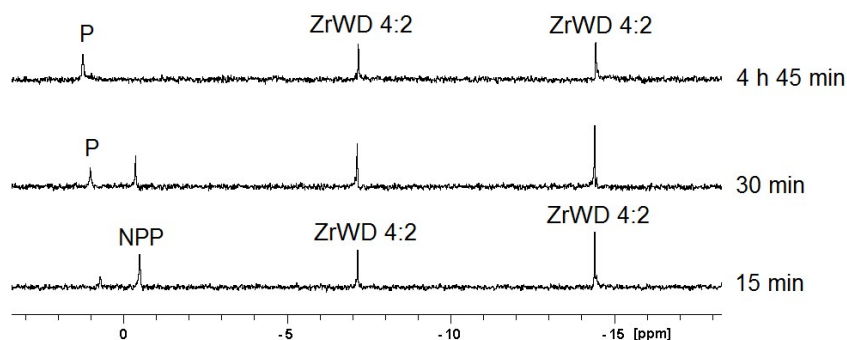


Figure S6. ^{31}P NMR spectra of the hydrolysis reaction of 5.0 mM of NPP in the presence of 3.0 mM of ZrWD 4:2 at different time intervals at pD 6.4 and 50 °C. (400 MHz, D_2O , 293 K, NS = 256, 25% H_3PO_4).

Table S4. Rate constant of each reaction cycle for 5.0 mM of NPP hydrolysis in the presence of 1.0 mM ZrWD 4:2 at pD 6.4 and 50 °C

The order number of reaction cycle	k_{obs} (10^{-5} s^{-1})	Rate enhancement
1	8.44 ± 0.36	/
2	21.96 ± 1.53	2.60
3	23.32 ± 2.57	2.76

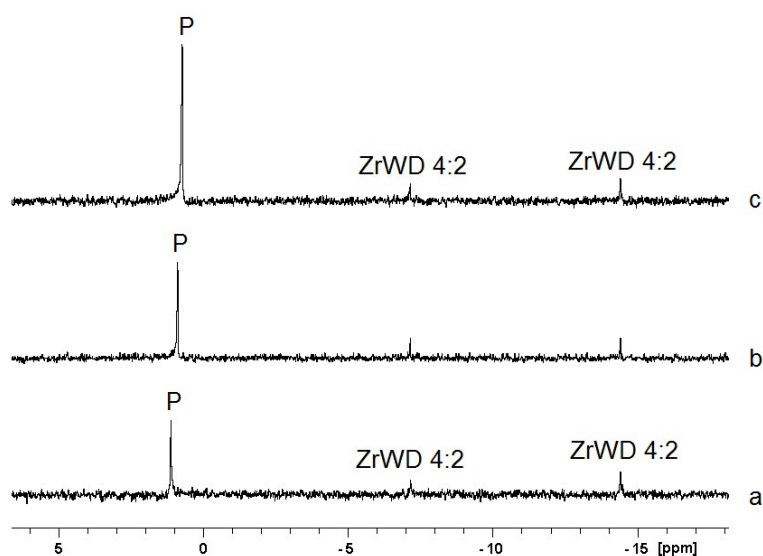


Figure S7. ^{31}P NMR spectra of the mixture reaction of 5.0 mM of NPP in the presence of 1.0 mM of ZrWD 4:2 after the first (a), the second (b) and the third (c) fully hydrolyzed reaction cycle at pD 6.4 and 50 °C. (400 MHz, D_2O , 293 K, NS = 256, 25% H_3PO_4).