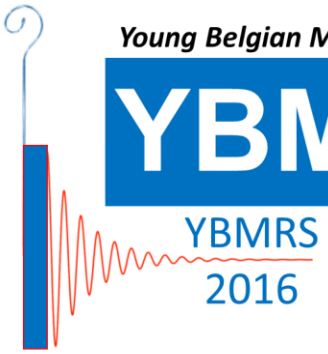

Young Belgian Magnetic Resonance Scientists

YBMRS 2016

15th edition

5th and 6th December 2016

PROGRAM AND ABSTRACT BOOK

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

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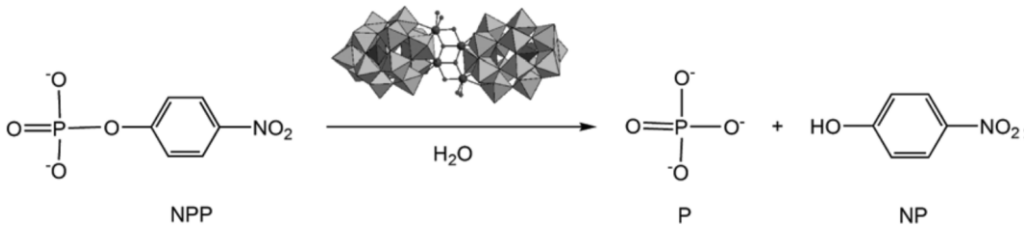
The detailed kinetic study of catalytic hydrolysis of a phosphoester bond in the DNA-model substrate 4-nitrophenyl phosphate (NPP) promoted by Zr^{IV}-substituted Wells-Dawson type polyoxometalate $Na_{14}[Zr_4(P_2W_{16}O_{59})_2(\mu_3\text{-}O)_2(OH)_2(H_2O)_4]\cdot 57H_2O$ (ZrWD 4:2) was followed by means of ^{1}H and ^{31}P NMR spectroscopy. The hydrolytic reaction proceeded with a rate constant of 8.44 (±0.36) × $10^{-5}s^{-1}$ at pD 6.4 and 50 °C, representing a 300-fold rate enhancement in comparison with the spontaneous hydrolysis of NPP (k_{obs} = 2.81 (±0.25) × 10^{-7} s^{-1}) under the same reaction conditions. The ZrWD 4:2 was also active towards hydrolysis of the more stable DNA-model substrate bis(4-nitrophenyl) phosphate (BNPP) and the RNA model substrate 2-hydroxypropyl-4-nitrophenyl phosphate (HPNP). The pD dependence profile of k_{obs} shows that the rate constants for NPP hydrolysis decrease significantly when the pD values of the reaction mixtures increase. The formation constant (K_f = 190 M^{-1}) and catalytic rate constant (k_c = 6.40 × 10^{-4} s^{-1}) for the NPP-ZrWD 4:2 complex, activation energy (E_a) of 110.15 ± 7.06 kJ mol^{-1}, enthalpy of activation ($\Delta H^{\ddagger}$) of 109.03 ± 6.86 kJ mol^{-1}, entropy of activation ($\Delta S^{\ddagger}$) of 15.20 ± 2.49 J mol^{-1} K^{-1}, and Gibbs activation energy ($\Delta G^{\ddagger}$) of 104.32 ± 6.09 kJ mol^{-1} at 37 °C were calculated from kinetic studies. The recyclability of ZrWD 4:2 was examined by adding an extra amount (5.0 mM) of NPP twice to a fully hydrolyzed mixture of 5.0 mM NPP and 1.0 mM ZrWD 4:2. The interaction between ZrWD 4:2 and the P–O bond of NPP was evidenced by a change in the ^{31}P chemical shift of the ^{31}P atom in NPP upon addition of ZrWD 4:2. Based on ^{31}P NMR experiments and the kinetic studies, a mechanism for NPP hydrolysis promoted by ZrWD 4:2 has been proposed.[1-4]



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