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Detailed Mechanism of ATP Hydrolysis Promoted by a Binuclear Zr^{IV} -Substituted Keggin Polyoxometalate Elucidated by a Combination of ^{31}P , ^{31}P DOSY and ^{31}P EXSY NMR Spectroscopy

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The full reaction mechanism of adenosine triphosphate (ATP) hydrolysis in the presence of the binuclear Zr^{IV} -substituted Keggin type polyoxometalate $(\text{Et}_2\text{NH}_2)_8[\{\alpha\text{-PW}_{11}\text{O}_{39}\text{Zr}(\mu\text{-OH})(\text{H}_2\text{O})\}_2]\cdot 7\text{H}_2\text{O}$ (ZrK 2:2) at pD 6.4 and 50 °C was elucidated by a combination of ^{31}P , ^{31}P DOSY and ^{31}P EXSY NMR spectroscopy, demonstrating the potential of these techniques for the analysis of complex reaction mixtures involving polyoxometalates (POMs). ^{31}P and ^{31}P DOSY NMR measured for pure ZrK 2:2 and for the solution containing ZrK 2:2 and ATP at pD 6.4 shows that in the presence of ATP, ZrK 2:2 converts into the more active species ZrK 1:1 and this species is responsible for the hydrolysis of the phosphoanhydride bonds.¹ Two possible parallel reaction pathways were proposed on the basis of the observed reaction intermediates and final products. The ^{31}P spectrum of a mixture of 20.0 mM ATP and 3.0 mM ZrK 2:2 at pD 6.4 measured immediately after sample preparation, shows the formation of a complex I1A and I1B between ATP and POM. During the course of the hydrolytic reaction at pD 6.4 and 50 °C, various products including adenosine diphosphate (ADP), adenosine monophosphate (AMP), pyrophosphate (PP) and phosphate (P) were detected. In addition, several intermediate species representing ADP/ZrK 1:1 (I2), AMP/ZrK 1:1 (I3), P/ZrK 1:1 (I4) and PP/ZrK 1:1 (I5) complexes were also identified. ^{31}P EXSY NMR spectra evidenced slow exchange between ATP and I1A, ADP and I2, and PP and I5.



1. T. K. N. Luong, P. Shestakova, T. T. Mihaylov, G. Absillis, K. Pierloot and T. N. Parac-Vogt, *Chemistry – A European Journal*, 2015, **21**, 4428-4439.