

## KINETIC AND MECHANISTIC STUDIES ON PHOSPHOESTER CLEAVAGE BY TETRAVALENT URANIUM SPECIES

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The rate constants of phosphoester hydrolyses catalyzed by tetravalent uranium ( $U(IV)$ ) species in aqueous solutions were determined using UV-vis spectroscopy. A variety forms of  $U(IV)$  species ( $U^{4+}(aq)$ ,  $UO_2(cr)$ -nanoparticles (NPs),  $U(IV)$ -oxalate( $ox$ )<sub>2</sub>,  $U(IV)$ -NPs-polyvinylpyrrolidone (PVP)) were prepared to assess their catalytic activity toward *p*-nitrophenyl phosphoester (NPP) cleavage at a wide range of pH (3-10). The prepared  $U(IV)$  species mediate the hydrolysis of NPP in aqueous solutions with rate enhancements compared to the uncatalyzed reactions. Interestingly,  $U(IV)$ -NPs is revealed as the most efficient catalyst for the hydrolysis of NPP among the other forms of  $U(IV)$  catalysts at pH 3-10. This result explains the proposed mechanism of this catalytic reaction that is mediated by the solid phase of the reaction medium.

### I. INTRODUCTION

In deep groundwater systems,  $U(IV)$  is a dominant redox form of uranium because of an anaerobic condition. Thus, it is very important to understand the behaviors of  $U(IV)$  interacting with organic molecules in order to assess the geological migration of actinide species in the groundwater environment [1].

Although many lanthanide and transition metal cations have been investigated as catalysts for the hydrolysis of phosphoesters, soluble and insoluble  $U(IV)$  species has not. This prompted us to try to generate the series of  $U(IV)$  species to explore their catalytic activities and hydrolytic mechanisms.

### II. RESULTS AND DISCUSSIONS

In order to quantitatively evaluate  $U(IV)$  relative to  $Ce(IV)$  promoters of phosphoester cleavage, we have determined the reactivity of  $U(IV)$  toward NPP and additional substrates (bis(*p*-nitrophenyl)phosphate (BNPP), *O,O*-Dimethyl *O*-(4-nitrophenyl) phosphate (paraoxone-methyl)). Substrates were hydrolysed readily in the present  $U(IV)$  catalysts. Reaction conditions comprised 50  $\mu$ M substrates and 100  $\mu$ M  $U(IV)$  catalysts in 0.1 M  $NaClO_4$  solution at pH 3-10 at both 25 and 50 °C. We employed a 2-fold excess of catalysts over substrates which is much smaller amount relative to the previous papers [2-4]. In the previous works, a 20-fold excess of catalysts was added to speed up the hydrolysis. The high concentration of metal catalyst, however, causes the precipitation of catalyst at high pH ranges.

Kinetics were followed spectrophotometrically, monitoring the disappearance of the substrates (290 nm) and the appearance of *p*-nitrophenol (NP) (317 nm) or *p*-nitrophenolate (400 nm).  $U(IV)$  catalysts mediate the cleavage of substrates is at least  $ca. 10^5$  times greater than the for the uncatalyzed reaction. Moreover, the  $U(IV)$  catalyzed hydrolysis is also  $ca. 3 - 4$  times faster than  $Eu^{3+}$  and  $Tm^{3+}$  catalyzed cleavage in the similar conditions.  $U(IV)$ -NPs, comparable to  $Ce(IV)$ , are generally more active than  $U^{4+}(aq)$ ,  $U(IV)Ox_2$  and  $U(IV)$ -NPs-PVP. This phenomenon can be explained by the solid-phase reaction mechanism. It seems that the substrates are strongly bound to the surface of nanoparticles which possess the hydroxide ions on the surface.

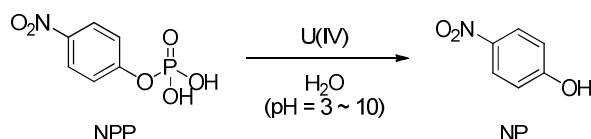


Fig. 1. Hydrolysis of NPP catalyzed by  $U(IV)$

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