

# Kinetic and Mechanistic Studies on Phosphoester Cleavage by Tetravalent Uranium Species

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## 1. Introduction

In deep groundwater systems, tetravalent uranium (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.

## 2. Results and Discussions

The rate constants of phosphoester hydrolyses catalyzed by U(IV) species in aqueous solutions were determined using UV-vis spectroscopy. A variety of 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).

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-

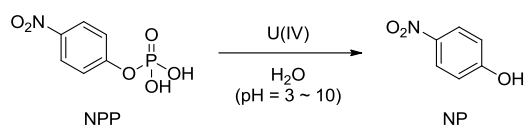


Fig. 1. Hydrolysis of NPP catalyzed by U(IV).

(IV) catalysts. Reaction conditions comprised 50  $\mu$ M substrates and 100  $\mu$ M U(IV) catalysts [2] in 0.1 M NaClO<sub>4</sub> 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 previous papers [3-5]. 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). Rate constants, *k* for NPP hydrolyses mediated by U(IV) species, appear in Table 1, where kinetic data for comparable hydrolyses catalyzed by cerium(IV) ammonium nitrate (Ce(IV)-AN) are also collected.

Table 1. Kinetics of the U(IV) and Ce(IV) catalyzed hydrolysis of NPP

Catalyst	T (°C)	$k_{obs}/10^{-4} s^{-1}$			
		pH 3	pH 5	pH 7	pH 9
U(IV)-NPs	25	1.18	1.38	1.72	0.761
	50	30.8	35.5	27.4	2.22
$U^{4+}$	25	0.71	0.61	0.50	0.273
	50	30.8	35.5	27.4	2.22
U(IV)-NPs-PVP	25	1.05	1.38	1.52	0.982
	50	28.3	34.6	35.4	2.40
U(IV)- $ox_2$	25	0	0	0.463	0.227
	50	0	0	1.50	0.68
Ce(IV)-AN	25	15.3	23.8	19.0	16.1
	50	89.4	128	102	89.4

It is revealed that U(IV) catalysts mediate the cleavage of substrates is at least *ca.*10<sup>5</sup> times greater

than the for the uncatalyzed reaction ( $k_{\text{obs}} = 3.3 \times 10^{-8} \text{ s}^{-1}$ ). Moreover, the U(IV) catalyzed hydrolysis is also *ca.* 3 - 4 times faster than  $\text{Eu}^{3+}$  and  $\text{Tm}^{3+}$  catalyzed cleavage in the similar conditions. Interestingly, U(IV)-NPs and U(IV)-NPs-PVP are comparable to Ce(IV), and they are generally more active than  $\text{U}^{4+}(\text{aq})$  and U(IV)- $\text{ox}_2$ . Such high catalytic activity can be explained by the solid-phase reaction mechanism. The reaction seems to undergo via strong binding of substrates to the surface of nanoparticles which possess the hydroxide ions on the surface.

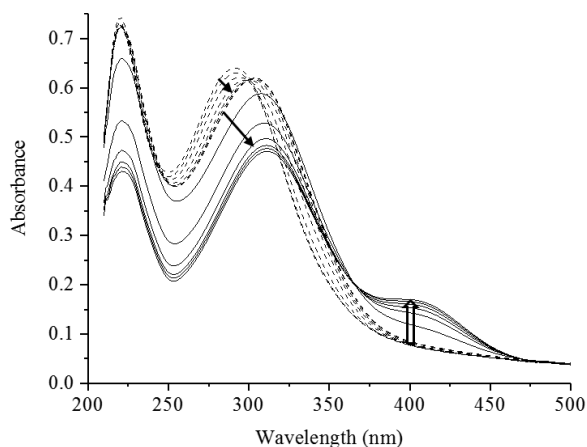


Fig. 2. UV-Vis absorption spectra of the NPP hydrolysis catalyzed by U(IV)-NPs at 50 °C monitored for 600 s (dash lines : 2-30 s, solid lines : 100-600 s).

In fact, formation of metal-phosphoester complexes occurs at the initial stage of the hydrolysis reactions, which is more evident at higher pHs. The UV-Vis absorption spectra in Fig. 2 shows that the U(IV)-NPP complexes are likely produced in the very beginning of the reaction, in 30 s (dash lines). Such complexation allows further increasing of the efficiency of the hydrolysis and suggests the possibility of two-step reaction mechanism: the formation of the complex (fast) and the cleavage of phosphoester bond (rate determining step).

### 3. Conclusion

Various U(IV) species were prepared to study the reaction kinetics and mechanism of the phosphoester cleavage. 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. The proposed mechanism in this study concludes that these catalytic reactions are mediated by the solid phases or NPs dispersed in the reaction medium.

### ACKNOWLEDGMENTS

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