

Ph.D. DISSERTATION DEFENSE

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Degree:	Doctor of Philosophy
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Date:	Wednesday, April 23 rd , 2025
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Title:	Mechanisms of Dechlorination and Denitration during Alkaline Hydrolysis of Polychlorinated Polynitrobenzenes
Chairperson:	Dr. Xiaoguang Meng, Department of Civil, Environmental, and Ocean Engineering, School of Engineering and Science
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ABSTRACT

This research studied the alkaline hydrolysis of the polychlorinated polynitrobenzene (PCPNB) 1,2,3,5-tetrachloro-4,6-dinitrobenzene (T_4), incorporating experimental and computational techniques to describe the kinetics, products, and mechanisms of hydrolysis. In addition to dechlorination and denitration, the impact of deprotonation of the hydrolysis byproducts was also investigated.

T_4 hydrolysis followed pseudo-first-order kinetics, with efficacy enhanced by increased pH and temperature. At 95°C, nearly all T_4 degraded within 30 minutes, compared to only 32% of T_4 after 8 hours under ambient conditions. Estimated half-lives of T_4 were determined to be 36.5 hours at pH 12 and 22°C, 35.5 minutes at pH 14 and 22°C, and 5.8 minutes at pH 12 and 95°C. Pseudo-first-order kinetic rate constants were calculated to be 0.050 h⁻¹ at pH 12 and 1.171 h⁻¹ at pH 14. Similarly, the rate constants were found to be 0.019 h⁻¹ at 22°C and 7.176 h⁻¹ at 95°C. There was a marked preference for dechlorination over denitration, attributed to chlorine's (Cl) superior leaving propensity and the larger electrostatic interactions with hydroxide (OH⁻). While dechlorination and denitration occurred simultaneously at the onset of hydrolysis, Cl groups were notably released more rapidly than nitro groups (NO₂), and temperature's impact on the process was found to be significant. After 24 hours at 95°C, there was an average release of 1.17 mM chloride (Cl⁻) per mM T_4 and 0.23 mM nitrite (NO₂⁻) per mM T_4 . Density function theory (DFT) calculations support the thermodynamic feasibility of bimolecular nucleophilic aromatic substitution (S_N2Ar), presenting a novel discovery where deprotonation of initial substitution products markedly increases subsequent substitution energy barriers. Specifically, deprotonation led to energy barrier increases of 7.3, 10.9, and 9.2 kcal/mol for the respective transformations of 1Cl_2 to 2Cl_2, 1Cl_2 to 1Cl1N_2, and 1N to 1Cl1N_2. In total, DFT calculations identified twelve (12) energetically favorable substitution products. Further, this research's findings—supported by electrospray ionization mass spectrometry (ESI-MS) and batch experiments—suggest that mono-substituted, deprotonated polychlorinated polynitrophenols (PCPNPs) are the dominant products.

The results and conclusions of this research contribute valuable theoretical insights into PCPNB alkaline hydrolysis and advance our understanding of the compounds' environmental fate.