

Computational investigation into the mechanism of a palladacycle-catalyzed decomposition of phosphorothioate triesters in methanol

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Sulfur-containing organophosphate triesters such as fenitrothion (*O,O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate) are potent insecticides that inhibit cholinesterases and pose potential health and ecological threats due to environmental accumulation. These risks merit the development of methodologies for their bulk destruction. Here, the mechanism of the palladacycle-catalyzed methanolytic cleavage of phosphorothioate triesters is investigated. The relationship between experimentally-determined k_2 vs. leaving group pK_a (Brønsted plot) shows a downward break at ${}^s pK_a = \sim 13$, indicating a change in rate-determining step with the two domains having β_{lg} values of 0.0 ± 0.03 and -1.93 ± 0.06 . A density functional theory investigation supports the mechanism in which substrates with good leaving groups (${}^s pK_a < 13$) proceed *via* rate-limiting substrate binding, while for poor leaving groups the rate-determining step involves leaving group departure. The calculations also predict a stable 5-coordinate thiophosphorane intermediate.