

Intramolecular Oxidation Pathway in the Hydroperoxidolysis of O,S-Dimethyl Methylphosphonate

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O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate is one of the most well known and toxic chemical warfare agents, causing convulsions and death in as few as 15 minutes by irreversibly inhibiting acetylcholinesterase. Due to its stability and non-volatile nature, it is also one of the most difficult to destroy. Because of its immense toxicity, it is imperative that VX is destroyed in as efficient a manner as possible. For VX to be neutralized, the P-S bond must be cleaved. Hydrolysis in alkaline solution results in the cleavage of both the P-S and P-O bonds in a 7:1 ratio. Unfortunately, the product of the P-O cleavage remains highly toxic. Destruction of VX via hydroperoxidolysis results in a much higher rate of cleavage of the P-S bond. Previous quantum mechanical calculations in the gas phase revealed an intramolecular oxidation pathway that cleaves the P-S bond and is favored by a ratio of approximately 600:1 over cleavage of the P-O bond. However, it is unclear whether this oxidation pathway is an artifact of the gas-phase conditions. Solution-phase calculations have been carried out using the M06-2X/6-31+G(d,p) level of theory and the SM8 continuum solvation model to provide a more accurate understanding of the feasibility of this unique pathway.