Neurotoxin Degradation and Phosphorus Recovery by Molybdenum(VI) Complexes Through Heterogeneous and Homogeneous Catalysis

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This is the first report of metal complexes that promote the degradation of sulfur-containing organophosphate neurotoxins with the benefits of heterogeneous catalysis and phosphorus recovery. Three strategies are presented that begin with a supported molybdenum(VI) peroxide polymer (Mo-Y(s)) made from the immobilization of a Mo(s)/H₂O₂(aq) mixture on a tetraammine-polystyrene support. The Mo-Y(s) support degrades phosphorothioate pesticides, and one of the products, diethyl phosphite, is a commodity chemical; this transformation represents a form of phosphorus recovery in organophosphate degradation. Specifically, Mo-Y(s) degrades phosphorothioate pesticides of the form (EtO)₂P(=S)(OAr) that include parathion, coumaphos and diazinon. Two common themes in this ethanolysis are the production of diethyl phosphite ((EtO)₂P(=O)H) and the corresponding oxon ((EtO)₂P(=O)(OAr)). In connection with diethyl phosphite production, various strategies (i.e. solvent, nature of phosphorothioate) will be presented that favor phosphite production over the oxon byproduct. In addition, preliminary mechanistic results suggesting peroxide attack on the phosphorothioate will be highlighted.

The second strategy uses the Mo-Y(s) polymer towards the ethanolysis of the VX analog O,S – diethylphenyl phosphonothioate (DEPP). In addition to the operational advantages of heterogeneous reactivity, the ethanolysis with H₂O₂ yields only P – S bond scission to yield diethylphenyl phosphonate and ethyl sulfate. The Mo-Y(s) polymer is regenerated by incubation in 30% H₂O₂(aq) which adds to the operational advantage of this supported molybdenum(VI) peroxy polymer. Activation parameters of DEPP ethanolysis by Mo-Y(s) and by the model compound oxodiperoxo(pyridine-2-carboxylato)molybdate(VI) are almost identical for the oxidation of thioanisole. This suggests the rate determining step for DEPP ethanolysis is sulfur oxidation to form an intermediate phoshonothioate S-oxide that subsequently undergoes nucleophilic attack by the ethanol solvent to form diethylphenyl phosphonate and ethyl sulfate.

The third strategy entails catalytic hydrolysis of DEPP by the monomeric MoO₄²⁻ molybdate; this is the first case of homogeneous phosphonothioate hydrolysis by a high oxidation state group VI complex under mild conditions (pH 7, 30 °C). Hydrolysis by MoO₄²⁻ yields ethylphenyl phosphonate resulting from exclusive P – S scission which is the preferred bond cleavage. The mechanism for this hydrolysis was modeled with density functional theory methods. In this scheme the oxoanion of MoO₄²⁻ attacks the phosphorus center of DEPP in a S₉2(P) fashion to form a mixed molybdate-phosphonate anhydride intermediate; this is followed by rapid hydrolysis. DFT calculations at the G++(d,p) level indicate this nucleophilic route is a viable pathway for the catalytic hydrolysis of DEPP by MoO₄²⁻. The initial S₉2(P) nucleophilic attack was successfully modeled that included a transition state search. Taken together, these three reports are the first case of group VI metal complexes that catalytically degrade sulfur-containing organophosphate neurotoxins. The degradation has the operational advantages of heterogeneous catalysis as well as phosphorus recovery to regenerate a commodity chemical.

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