Examination of the Hydroperoxidolysis of a VX Model Compound

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VX Facts

• Discovered by various groups in 1952–53
• It is mistaken by the body to be acetylcholine, a neurotransmitter that causes muscles to contract
• Previous research has shown that VX is best neutralized by an attack of hydroperoxide
Model VX–Compound

O-ethyl S-2-[(diisoproylamino)ethyl] methylphosphonothiolate (VX)

O,S-dimethyl methylphosphonothiolate
Previous Research
Oxygen Transfer

• This shift was found to be the pathway requiring the least energy
• This, however, is suspect since the transfer is so unusual
• The goal of this research is to learn more about the oxygen transfer and determine its likelihood
Theory

- MPWB1K/6-31+G(d,p)
  - Provides accurate representation of energies and geometries (quantum)
- Standard quantum chemical results are obtained at 0 K
- Thermal energy can be considered by employing classical molecular dynamics
ADMP Calculations

- Atom-Centered Density Matrix Propagation
  - Treats electrons quantum-mechanically, but nuclei classically

\[ F = ma = m \frac{dv}{dt} = m \frac{d^2x}{dt^2} = -\frac{\partial}{\partial r} U \]

*U* is the energy from the quantum calculation
Generates a thermal potential energy surface
A gas–phase reaction can have a potential energy surface (PES) that is very different from the PES of the same reaction in solution.
Motivation

- Previous study employed gas-phase geometries
- Current study employs gas-phase conditions as well as aqueous conditions.
- Solvation could have significant impact on results
Gas Phase Results

- The observed outcomes of gas phase
  - TBP
  - Direct P–S cleavage
  - Rearrangement with loss of water
  - Rearrangement with loss of OH group (possibly additional water)
- Only the TBP product was previously predicted
- Suggests a more complicated PES than originally thought
To view movie: [http://jade6.truman.edu/movies/tbr.mov](http://jade6.truman.edu/movies/tbr.mov)
Direct P–S Bond Cleavage

To view movie:
http://jade6.truman.edu/movies/ps.mov
Formation of $\text{H}_2\text{O}$

To view movie:
http://jade6.truman.edu/movies/water.mov
Gas Phase Summary

One Hundred completed trajectories:

- TBP: 16.0% (16)
- OH: 6.0% (6)
- P-S: 33.0% (33)
- H₂O: 45.0% (45)
Aqueous Phase Results

- Stationary point calculations have led to an acceptable transition state.
- Frequency calculations were used to pinpoint the most stable geometry.
- From this, subsequent ADMP calculations can be performed.
- This will follow the same procedure as the gas phase.
Aqueous Transition State

- This is the optimized geometry from which ADMP calculations will start
Goals for the Future

- Using the constructed aqueous transition state, determine the existence of the oxygen transfer
- Continue to collect aqueous phase data using ADMP calculations
- Use combined data to confirm most probable mechanism for the hydroperoxidolysis of VX
References and Special Thanks

• References

• Special Thanks
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