Computational Chemistry Modeling of the Atmospheric Fate of Toxic Industrial Compounds (TICs)

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Abstract

This paper describes the application of high performance computing to the prediction of the rate constants of reactions occurring in the troposphere involving toxic industrial compounds. The methods we employ use a combination of quantum chemistry and quantum dynamics to calculate the kinetics of the reactions under investigation. Our accomplishments from the past year are presented and discussed.

1. Introduction

The ability to accurately and confidently compute the kinetics of potentially significant atmospheric reactions of toxic industrial compounds (TICs) is a critical component of Department of Defense (DoD) chem/bio defense programs as well as Homeland security. However, much of the critical kinetic data (e.g., rate constants for target reactions) does not exist and is difficult and expensive to obtain experimentally. Our unique approach is to use state-of-the-art computational quantum chemistry/ quantum dynamics models to compute rate constants which can then be directly input into atmospheric chemistry modules within DoD transport and dispersion (T&D) models. To this end, T&D models, such as SCIPUFF and the recently parallelized ChemCODE/ ChemCONC (Common High Performance Computing Software Support Initiative project CBD-03) have been updated with the ability to model atmospheric degradation of released toxic chemicals. This addition has resulted in the improved ability of the models to handle the fate and interaction of TICs in the atmosphere, resulting in a more realistic representation of the contamination zone. The methods we apply can be used not only to predict the changing health threat in both an urban and battlefield environment, but can also predict the nature of the resulting byproducts. This information would be valuable in programming advanced sensors to warn of the release of a toxic compound even if the material has degraded by the time it reached the detection array. In addition, the results of these calculations can also be used to make a more scientifically defensible selection of simulants for challenging detectors, as well as assisting in the evaluation of both individual and collective protection systems. These calculations will also be used to provide a sound theoretical underpinning to the development of physical properties data, which is critical for choosing the proper simulant for use in synthesis, fate, and decontamination studies, as well as in the assessment of new potential threat agents and the selection of improved decontamination concepts.

2. Methodology

A team of approximately seven PhD level computational scientists at the US Air Force, US Army Research Laboratory (ARL), ENSCO, Inc. in Melbourne,

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FL, and BWD Associates in Gainesville, FL, has demonstrated that accurate rate constants can be calculated using a combination quantum chemistry/quantum dynamics (QC/QD) approach. This method is computationally intensive; it requires the use of high level *ab initio* quantum chemistry to calculate accurate structures of molecules at the various important stationary points along the minimum energy path that connects reactants to products. The computed energies of the various stationary points are also critically important. An error of ±0.4 kcal/mol in the computed kinetic barrier height (the difference in the computed energies of the saddle point and reactant) can lead to a doubling or halving of the computed rate at 298K. This clearly shows that sub-kcal/mol accuracy is required of this energy difference, which is by current QC standards, a very challenging constraint. To achieve this level of accuracy, we use an energy extrapolation which accounts for the well understood and predictable deficiencies in the QC methods used.

Additional information characterizing the transition state is also needed; i.e., the negative (repulsive) CCSD curvature of the minimum energy path at the transition state. Since a full CCSD vibrational frequency calculation can not be completed in a timely manner, we compute the CCSD curvature of the repulsive mode at the transition state by fitting a harmonic potential to three CCSD single point energies (one at the transition state and one on each "side" of the transition state). In addition to the curvature of the repulsive mode, a description of the soft modes, in the neighborhood of the transition state, must also be known. Once again, the molecular size (i.e., number of atoms and number of basis functions) of the compounds under study precludes the use of coupled cluster theory to calculate this information. Instead, we use a neglect of diatomic differential overlap (NDDO) Hamiltonian that is reparameterized to accurately reproduce coupled cluster theory. Specifically, given the transition state geometry computed at the coupled cluster level and the curvature of the repulsive mode computed using the three point fit method, we vary the parameters of the AM1 variant of the NDDO Hamiltonian using a combination of simulated annealing and genetic algorithms such that the transition state geometry and the vibrational modes generated using the reparameterized NDDO Hamiltonian compare with those from coupled cluster theory. Finally, this information is provided as input to a newly developed Semi-Classical Flux-Flux Autocorrelation Function (SCFFAF) approach to chemical dynamics which computes the kinetic rate curve of the reaction under investigation over a wide temperature range. Details of this methodology can be found in Reference 1. In summary, the major steps required to compute a rate constant are as follows:

1. Identify compound and reaction to study.
2. Optimize reactant structures at MP2/6-31++G** level of theory to determine which conformations are energetically accessible at ambient temperature.
3. Using chemical intuition and the parent structures identified above, we generate guess structures of likely transition states and optimize at MP2/6-311++G**. This typically can result in up to as many as 30 potential transition states of interest.
4. Once the transition states structures have converged, the activation energy (energy of the transition state minus energy of reactants) for each converged transition state is determined. For those transition states that have an activation energy of ≤3 kcal/mol, we initiate a MP2/6-31++G** vibrational frequency calculation. This calculation serves a two-fold purpose: a) it verifies that the computed structure is indeed a first-order transition state (i.e., vibrational analysis contains one and only one repulsive mode) and b) generates a guess Hessian for the next series of calculations.
5. Optimize selected transition states and reactant structures at CCSD/6-31++G**.
6. Run the energy extrapolation calculations on the converged transition states and reactants.

The extrapolation method consists of the following:

- Single point energy: QCISD(T)/6-311g** (QCI)
- Single point energy: MP2/6-311g** (SML)
- Single point energy: MP2/6-311+G(3df,2p) (LRG)
- Zero Point Energy (ZPE) from a vibrational frequency analysis: MP2/6-31++G**

The extrapolated energy = E(QCI) + E(LRG) – E(SML) + ZPE

7. Compute the CCSD curvature of the transition state using the three point fit methodology.
8. Use the CCSD structure and curvature information to generate the Transfer Hamiltonian.
9. Run the Transfer Hamiltonian calculations to characterize the region around the CCSD/6-31++G** transition state.
10. Compute the kinetic rate curve using the SCFFAF methodology.

3. Results

During FY 07, we have calculated temperature dependent rates for the following hydrogen abstraction reactions:

- Reaction 1: Dimethyl phosphonate [DMHP, $(CH_3O)_2P(O)H$] + OH radical
- Reaction 2: Dimethyl methylphosphonate [DMMP, $(CH_3O)_2P(O)CH_3$] + OH radical
- Reaction 3: Diethyl methylphosphonate [DEMP, $(CH_3CH_2O)_2P(O)CH_3$] + OH radical

In this manuscript we summarize the results of the DMHP reaction[2].

3.1. Reaction 1: DMHP + OH

When released into the troposphere, dimethyl phosponate (DMHP) will degrade, for example, by reacting with hydroxyl (OH) radicals. The products of this hydrogen abstraction reaction are a radical DMHP species and water. Our calculations found four transition states that are accessible at ambient temperatures and are thus the major contributors to the total rate. Figures 1–3 show three different transition states for the abstraction of a hydrogen atom from one of the methyl groups on DMHP. Figure 4 shows the transition state for the abstraction of the hydrogen atom that is bonded to the phosphorus atom. Figure 5 shows the computed temperature dependent rate constants for each of these mechanisms, as well as the total rate, which is simply the sum of the individual rates. Our calculated total rate agrees quite favorably with the experimental rate[3], shown in Figure 5. Note that each of the experimental data points is an individual measurement at a single temperature, whereas our calculations give the full temperature dependent rate.

4. Conclusions

When released into the troposphere, volatile organic compounds, such as the organophosphorus compounds studied here, typically react with OH radicals. In this work, we have used a combination of quantum chemistry and quantum dynamics to theoretically predict the temperature dependent rates for the abstraction of hydrogen atom atoms by OH radicals for a series of organophosphonates. These computed rate constants will be used as input into atmospheric chemistry modules within DoD T&D models, such as SCIPUFF and ChemCODE/ChemCONC. The addition of finite chemistry will result in the improved ability of the models to handle the fate and interaction of TICs in the atmosphere, resulting in a more realistic representation of the contamination zone.

References

1. Runge, K., and M.G. Cory, and R.J. Bartlett, "The Calculation of Thermal Rate Constants for Gas Phase Reactions: A Quasi-Classical Flux-Flux Autocorrelation function (QCFFAF) approach." *J. Chem. Phys.*, 114, 5141, 2001.

2. The results for the DMMP and DEMP reactions are in progress.

3. Aschmann, S.M.,E.C. Tuazon, and R. Atkinson "Atmospheric Chemistry of Dimethyl Phosphonate, Dimethyl Methylphosphonate, and Dimethyl Ethylphosphonate." *J. Phys Chem A.*, 109, 11828, 2005.

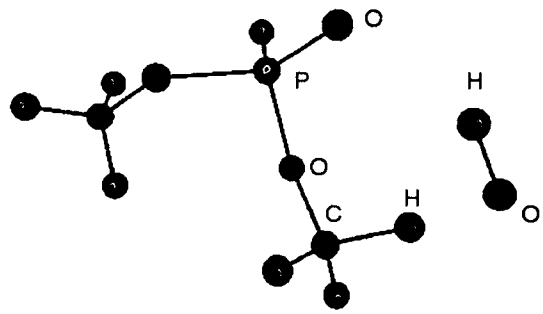

Figure 1. DMHP + OH TS1

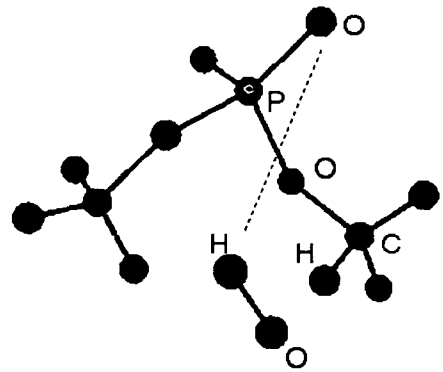

Figure 2. DMHP + OH TS2

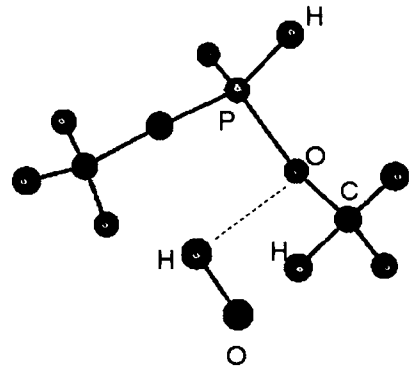

Figure 3. DMHP + OH TS2p

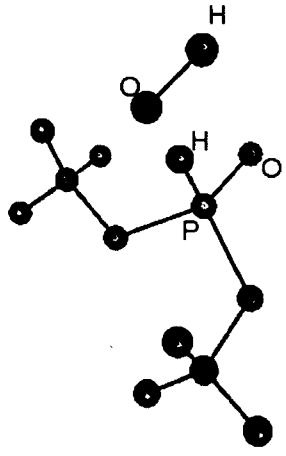

Figure 4. DMHP + OH TS3

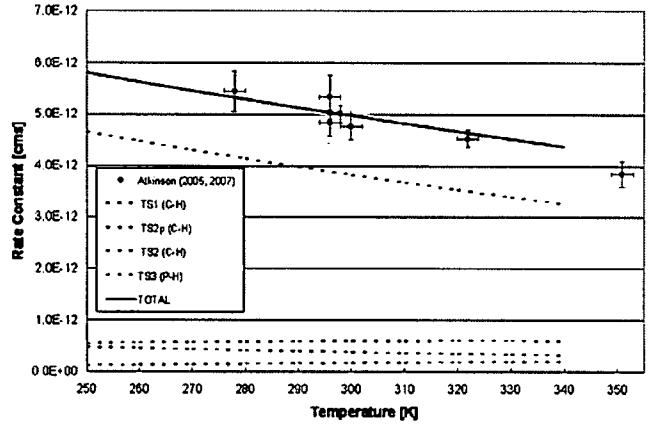

Figure 5. Temperature dependent rate constants for the reaction of DMHP + OH