

Characterization of High Explosives and Other Energetic Compounds by Computational Chemistry and Molecular Modeling

Experiments for the Undergraduate Curriculum

John A. Bumpus,* Anne Lewis, and Corey Stotts

Department of Chemistry, University of Northern Iowa, Cedar Falls, IA 50614; *john.bumpus@uni.edu

Christopher J. Cramer

Department of Chemistry and Supercomputing Institute, University of Minnesota, Minneapolis, MN 55455-0431

Heat of formation is one of a variety of properties used to assess and compare the energy content of high explosives¹ (1). We present a series of introductory and advanced experiments in which heats of formation are predicted from calculation. These experiments can be used to introduce students to commercially available computational chemistry and molecular modeling programs. They also help reinforce several concepts in thermodynamics and computational chemistry. In the initial experiment several compounds are arranged such that students are provided structures with increasing levels of complexity so that they may master the drawing programs in a stepwise manner. Ab initio quantum mechanical (QM) calculations are used to model simple compounds. However, as structural complexity increases, students quickly learn time and expense are considerations in the use of such calculations. In the second experiment students are shown how to set up and use semiempirical calculations, the Austin Model 1 (AM1), the Modified Neglect of Differential Overlap (MNDO) Model, and the Parametric Model 3 (PM3), to estimate the heats of formation for a series of energetic compounds, including some that are used as high explosives. In the third experiment, selected results from computational studies are compared with those predicted using an older, but still useful, group additivity method (2, 3). Both approaches are compared to experimental values. Explosive compounds selected for study range from the very simple (e.g., methane) to the moderately complex (HMX and octanitrocubane). Although the PM3 model proves reasonably accurate for most of the compounds studied, it is not suitable for highly strained compounds such as cubane and octanitrocubane. This deficiency is used in the fourth experiment to introduce a more rigorous theoretical treatment in which density functional theory (DFT) is coupled with an isodesmic reaction approach to calculate the heat of formation of octanitrocubane. The structures of several explosives are presented in Figure 1.

Experimental Procedures

The following series of in silico experiments have been developed to introduce students to molecular modeling and computational chemistry of high explosives and other selected energetic compounds. The first experiment is introductory in nature and serves the dual purpose of teaching students how to use available software and familiarizing them with the structures of the explosives and other compounds used

in these experiments. The remaining three experiments introduce students to new and old computational methods used to calculate heats of formation.

Experiment 1: Molecular Model Construction

Students are provided the structures of a number of high explosives and other selected energetic compounds and are asked first to draw them in any one of several molecular modeling programs that are commercially available. For example, we have available PC Spartan (Wavefunction, Inc.), HyperChem 7.0 (Hypercube, Inc.), and ChemDraw Standard 7.0, which is used in conjunction with Chem 3D Ultra 7.0 (CambridgeSoft Corp). Manufacturers of these software programs provide relatively straightforward instructions for

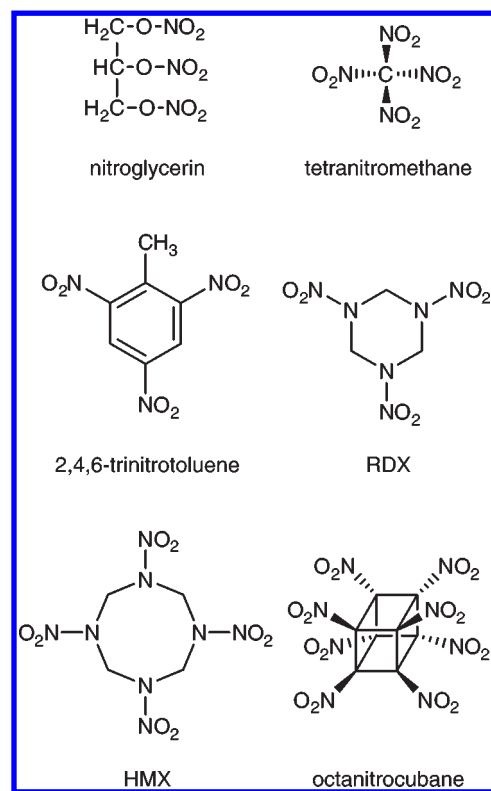


Figure 1. Structures of several highly energetic compounds.

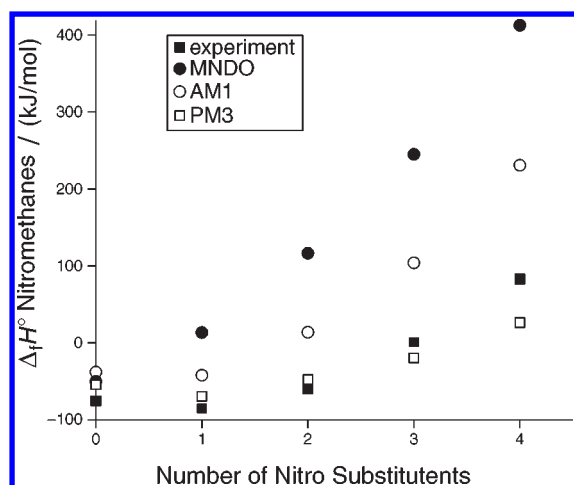


Figure 2. Heats of formation for methane, nitromethane, dinitromethane, trinitromethane, and tetranitromethane calculated using semiempirical procedures (AM1, PM3, and MNDO) and compared with experimental.

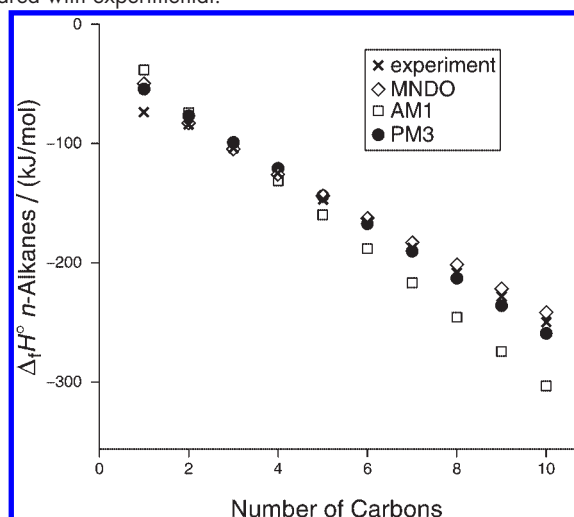


Figure 3. Heats of formation for *n*-alkanes (C_1 to C_{10}) calculated using semiempirical procedures (AM1, PM3, and MNDO) compared with experimental.

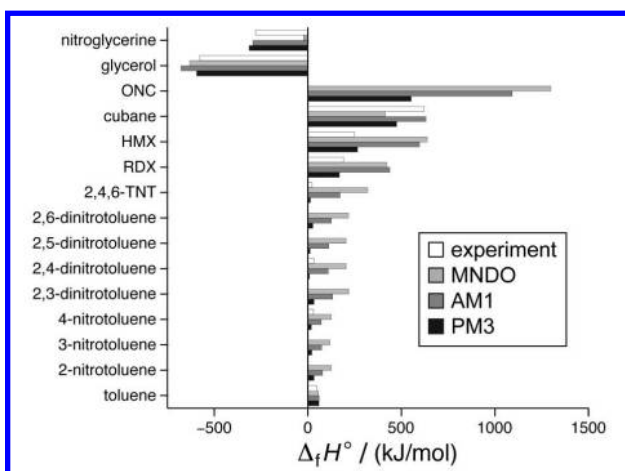


Figure 4. Heats of formation for toluene, mononitrotoluenes, several dinitrotoluenes, 2,4,6-trinitrotoluene, and several other high explosives. Heat of formation values were calculated using semiempirical procedures (AM1, PM3, and MNDO) and compared, where available, with experimental values.

their use. Thus, specific details are not provided here. Suffice it to say that all require a brief introduction by the instructor concerning their basic features. Ideally, this is accomplished in small groups. It is our experience that following brief instruction, most students have little problem with the rudiments of model construction. We also take this opportunity to demonstrate tools that allow the student to move the molecules in question so that they may be viewed from all angles thus providing a visual three dimensional image. At this point, students are taught how to minimize the energy of their molecular geometries. Bond angles and bond lengths from the optimized structures are compared with those determined experimentally. For this exercise, relatively less energetic compounds can also be used. We have elected to use a selection of C_1 to C_{10} hydrocarbons, alcohols, and several energetic compounds (i.e., high explosives, see Figure 1). In addition to structural considerations, we also request students to provide the length of time required for each calculation to impress upon them the rather dramatic increase in computer analysis time that accompanies increased structural complexity.

Experiment 2: Calculation of Heats of Formation Using Semiempirical Models

Students are asked to use three (MNDO, AM1, and PM3) semiempirical models to calculate heats of formation of several compounds (selected and assigned by the instructor) and to assess the accuracy of these models by comparing calculated values to experiment. Most of the experimental values of the compounds under investigation can be found on the NIST Web site (4). Students are shown how to consult and use this database to obtain experimental values and are thus introduced to this useful, easy-to-use (and free) on-line reference. Some of the required experimental heats of formation may not be available on the NIST Web site. In such cases, these values are provided or students are given guidance that will help them locate these values in the literature. *Lange's Handbook of Chemistry* (5) and *Thermodynamic Data of Organic Compounds* (6) are two good sources. Students are then asked to present experimental and calculated heats of formation in tabular and graphical forms. In the tables and graphs that are generated, experimental heats of formation are compared to calculated heats of formation obtained using the semiempirical models. Visual inspection of the table and graphs generated by the students are sufficient to conclude that the PM3 model provides the most reasonable overall calculations. Cubane was an exception to this generalization as the calculated heat of formation, 474.9 kJ/mol, of this highly strained aliphatic compound was substantially less than the experimentally determined value, 622.2 kJ/mol (7). Semiempirical (PM3) calculations for octanitrocubane, one of the new generation of high explosives, predicted a heat of formation of 552.7 kJ/mol. This value is within the rather broad range (339–728 kJ/mol) calculated by others using a variety of procedures (8). Although they may be useful in many instances it should be stressed that semiempirical methods are a first choice to calculate heats of formation primarily because they are rapid (i.e., less costly) compared to other computational procedures that use higher-level theory (e.g., ab initio and density functional theories). An example using a higher level of theory to calculate heat of formation of

octanitrocubane is provided in experiment 4. Figures 2–4 are examples of graphs that can be generated by students to compare experimental heats of formation with heats of formation calculated using semiempirical models.

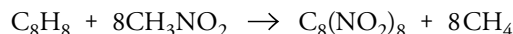
Experiment 3: Calculated Heats of Formation Using a Group Additivity Approach

The group additivity method of Benson and Buss (2) is a straightforward approach to calculating heats of formation for organic compounds. In favorable instances predicted values are within 4–8 kJ/mol of experimental values. In this experiment, students are provided group additivity bond contribution values and asked to calculate the heats of formation of a subset (chosen by the instructor) of the explosives and selected other compounds modeled in experiments 1 and 2. The heats of formation for *n*-alkanes, *n*-alcohols, and a few nitroalkanes are accurately predicted. Figures 5 and 6 are graphs comparing experimental heats of formation with heats of formation calculated using the group additivity method. Figure 7 compares experimental heats of formation with heats of formation calculated using group additivity and semiempirical models.

The group additivity method (2) is very effective for predicting heats of formation of *n*-hydrocarbons and *n*-alcohols. However, for highly strained systems (e.g., dinitromethane, trinitromethane, tetranitromethane, cyclobutane, cubane, and octanitrocubane) factors other than group additivity must be considered. For example, when applied to polynitro compounds such as dinitromethane, trinitromethane, and tetranitromethane, values estimated using the group additivity approach differ substantially from experimental values. Interestingly, the PM3 semiempirical model provides calculated values for most of these compounds that are reasonably close to experiment.

Experiment 4: Calculation of the Heat of Formation of Octanitrocubane: Isodesmic Reactions Coupled with a DFT Approach

Octanitrocubane is a new generation high explosive. Its heat of formation has not been determined experimentally and the use of the group additivity method and semiempirical methods are not suitable for determination of heats of formation of highly strained compounds. Early attempts to calculate the heat of formation of octanitrocubane resulted in values ranging from 339–602 kJ/mol (8). More recently, Zhang and Xiao (9) used DFT to calculate the heat of formation of octanitrocubane as 726.47 kJ/mol. In their investigation the heat of reaction for the following isodesmic reaction was calculated:



The calculated heat of reaction coupled with literature values for the heats of formation for methane, nitromethane, and cubane were used to calculate the heat of formation for octanitrocubane. Data used for this calculation are presented in the Supplemental Material^W, which is adapted from Zhang and Xiao (9). We have found that the model LSDA/pBP86/DN* found in SpartanPC DFT also provides reasonable data for these calculations. Data obtained using this model and level of theory are also presented in the Supplemental Material.^W

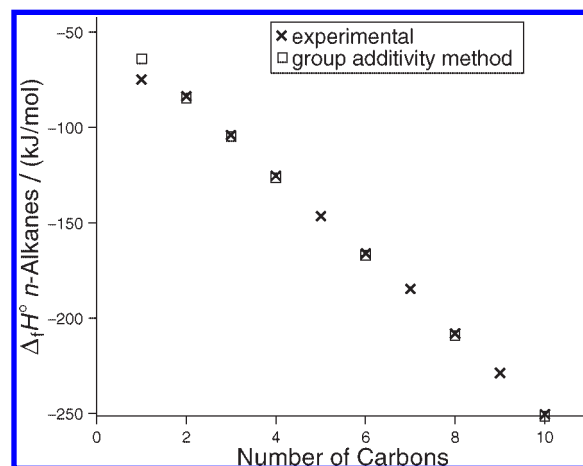


Figure 5. Heats of formation for *n*-alkanes (C_1 to C_{10}) calculated using the group additivity method compared with experimental.

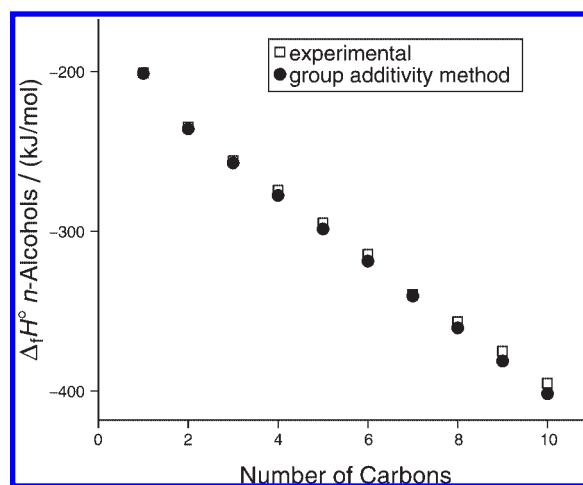


Figure 6. Heats of formation for *n*-alcohols (C_1 to C_{10}) calculated using the group additivity method compared with experimental.

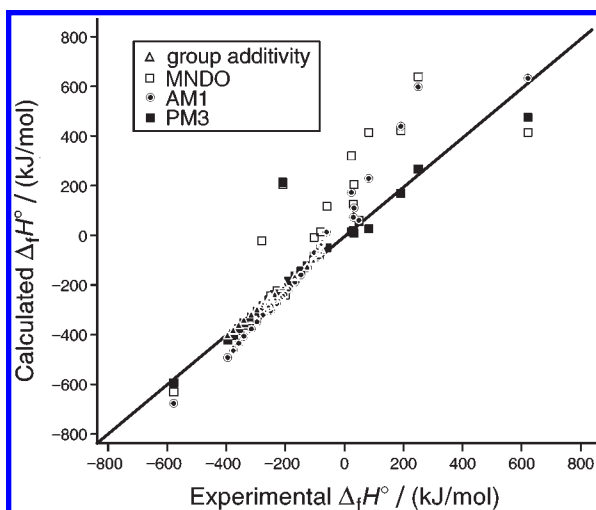


Figure 7. Heats of formation for selected compounds. Heats of formation were calculated using the group additivity method and semiempirical procedures (AM1, PM3, and MNDO) and compared with experimental. Compounds whose heats of formation were calculated and used include those compounds in Figures 1, 2, and 6 as well as the C_1 to C_{10} *n*-alkanes and *n*-alcohols.

Hazards

There are no significant hazards in this experiment.

Summary

Certain physical and chemical properties of energetic aliphatic and aromatic compounds can be used to predict their usefulness as explosives. Computational chemistry and molecular-modeling procedures may be applied to predict some of these same properties. We describe experiments suited for the undergraduate instructional laboratory in which the heats of formation of several compounds are calculated using semiempirical procedures. Three semiempirical models, AM1, MNDO, and PM3, were evaluated. In general PM3 proved most successful in its ability to predict the heats of formation of the energetic compounds studied when compared to experimental data. Cubane was an exception. The calculated heat of formation (474.97 kJ/mol) of this highly strained aliphatic compound was substantially less than the experimentally determined (622.2 kJ/mol) value. Semiempirical (PM3) calculations for octanitrocubane, a new high explosive, predicted a heat of formation of 552.7 kJ/mol. This value is within the rather broad range (339–728 kJ/mol) calculated by others using a variety of procedures. However, it is substantially less than presumably more accurate values calculated using an isodesmic approach coupled with density functional theory.

Acknowledgments

JAB, AL, and CS received support from the National Science Foundation under grants No. CHE-0137438 (RSEC Site Award) and CHE-0203346.

Supplemental Material

For each experiment, instructions for students and notes for the instructor are available in this issue of *JCE Online*.

Notes

1. High explosives, such as 2,4,6-trinitrotoluene, exhibit detonation velocities ranging from 1006 m/s (3300 feet per second) to 8839 m/s (29,000 feet per second). Low explosives, such as black powder, tend to deflagrate (burn) rather than detonate at velocities less than 1006 m/s. The cut off speed between high and low explosives is arbitrary.

Literature Cited

1. Akhavan, J. *The Chemistry of Explosives*; The Royal Society of Chemistry: Cambridge, 1998; p 173.
2. Benson, S. W.; Buss, J. H. *J. Chem. Phys.* **1958**, *29*, 546.
3. Benson, S. W.; Cruickshank, F. R.; Golden, D. M.; Haugen, G. R.; O'Neal, H. E.; Rodgers, A. S.; Shaw, R.; Walsh, R. *Chem. Rev.* **1968**, *69*, 279.
4. NIST Chemistry WebBook Home Page. <http://webbook.nist.gov/chemistry/> (accessed Oct 2006).
5. *Lange's Handbook of Chemistry*, 15th ed.; Dean, John A., Ed.; McGraw-Hill: New York, 1999; p 1424; formerly compiled and edited by Norbert Adolph Lange.
6. Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermodynamic Data of Organic Compounds*, 2nd ed.; Chapman and Hall: London, New York, 1986; p 792.
7. Kybett, B. D.; Carroll, S.; Natalis, P.; Bonnell, B. W.; Margrave, J. L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 3.
8. Zhang, M-X.; Eaton, P. E.; Gilardi, R. *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 401.
9. Zhang, J.; Xiao, H. *J. Chem. Phys.* **2002**, *116*, 10674.