RECEIVED
DEC 11 1997
OSTI

DOE/ER/14341--71

STUDY OF IMPROVED METHODS FOR PREDICTING CHEMICAL EQUILIBRIA

FINAL TECHNICAL REPORT

For Period April 1, 1993- August 31, 1997

Terry G. Lenz

Department of Chemical and Bioresource Engineering

And

John D. Vaughan

Department of Chemistry

Colorado State University

Fort Collins, CO 80523

October, 1997

Prepared for

**THE U.S. DEPARTMENT OF ENERGY
AGREEMENT NO. DE-FG03-93ER14341**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

808

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

Summary of Achievements for This Project

Background

A long-standing goal of chemical engineers and chemists has been the development of techniques for accurate prediction of the thermodynamic properties of isolated molecules. The thermochemical functions for an ideal gas then provide a means of computing chemical equilibria, and such computations can be extended to condensed phase chemical equilibria with appropriate physical property data. Such capability for predicting diverse chemical equilibria is important in today's competitive international economic environment, where bringing new products to market rapidly and efficiently is crucial. The purpose of this project has been to develop such computational methods for predicting chemical equilibria.

Current computational chemistry methods typically employ sophisticated computer programs capable of calculating the equilibrium properties of isolated molecules, such as detailed internal geometry, vibrational frequencies, dipole moments, steric energy, and thermodynamic properties. Models for computing the detailed equilibrium properties of isolated molecules may be divided into the following general categories:

- (i) *ab initio* treatments;
- (ii) semiempirical molecular orbital techniques;
- (iii) molecular mechanics or force field methods.

Both the *ab initio* and semiempirical molecular orbital methods seek to determine molecular properties by solving the molecular Schrödinger equation,

$$H\psi = E\psi.$$

Strict *ab initio* solution of the Schrödinger equation requires the true molecular Hamiltonian and does not depend upon empirical data; however, most *ab initio* models for multielectron systems employ approximations to the molecular Hamiltonian such as neglect of coulomb interactions and spin-orbit coupling. Semiempirical molecular orbital methods also use a simplified Hamiltonian and introduce explicit empiricism via coulomb and exchange integrals in some of the calculations. The primary reason for employing the semiempirical molecular orbital methods is that highly accurate *ab initio* calculations are at present not possible at reasonable cost for any but fairly simple molecular systems (six to eight heavy atoms). However, the semiempirical molecular orbital calculations themselves typically do not have sufficient accuracy (heats of formation within $\pm 4\text{kJ/mol}$ and heat capacity or absolute entropies to within $\pm 4\text{J/mol}\cdot\text{K}$ of experimental values) for thermodynamic calculations. Thus, if one is interested primarily in computations of thermodynamic accuracy for a fairly broad range of non-trivial molecules, the molecular mechanics or force field approach is the logical method of choice at the present time. Force-field modeling was therefore chosen as the basis of the present research. Although these force field models do involve empiricism, they are based upon firm molecular structure theory and are being continually improved as more fundamental results from *ab initio* calculations and additional high quality experimental data become available.

Specific Results

Achievements for this overall project include purely computational as well as experimental results. These results are briefly summarized below.

Computational Studies

1. A modified version of the Boyd MOLB3 force-field method has been employed to compute the structure, standard enthalpy of formation, and standard absolute entropy for a variety of dienes and unsaturated ring and methylene-bridged compounds. Results for 1,3-butadiene, 1,3-pentadiene, 1,3-cyclohexadiene, 1,3-cycloheptadiene, cyclopentene, norbornane, norbornene, norbornadiene, bicyclo[3.2.1]octane, bicyclo[3.3.1]nonane, and 1,3-cyclopentadiene were generally in excellent agreement (typically ± 1 kcal/mol for ΔH_f° , and ± 1 cal/(mol·K) for S°) with observed values and with calculations we and others have made with the Allinger MMP2 and Ermer-Lifson CFF-3 programs.
2. A force-field model was employed to calculate thermodynamic properties of the monomer and both endo and exo isomers for 1,3-cyclopentadiene dimerization at temperatures ranging from 273 to 500 K. Calculated equilibrium constants for both the gas and liquid phase, and other thermodynamic properties, agreed satisfactorily with what appeared to be somewhat inconsistent existing experimental data. This work thus illustrated that force-field methods hold promise as a useful alternative to experimental methods for the study of equilibrium properties of chemically reactive systems involving nontrivial molecules.
3. ΔH° , ΔS° , and K_p were calculated by force field methods for two prototype Diels-Alder reactions, the condensation of 1,3-butadiene and ethylene, and the dimerization of 1,3-butadiene. Three force field programs were employed, Allinger's MMP2, Warshel and Karplus' CFF/PI, and Boyd's MOLBD3 (with Anet and Yavari diene parameters). MMP2 and CFF/PI were combined to calculate reactant and product ΔH_f° (by MMP2) and thermodynamic functions S° , C_p° , and $(H_T^\circ - H_0^\circ)$ by use of CFF/PI molecular geometry and vibrational frequencies. MOLBD3 was used separately to calculate these properties. The combined MMP2, CFF/PI calculations exhibited excellent agreement with available experimental equilibrium data for both reactions, despite uncertainties in the number and energies of adduct conformers in the dimerization reaction. The MOLBD3 results were less satisfying, particularly for the dimerization reaction, because the entropy of 1,3-butadiene was overestimated by $2.5 \text{ cal mol}^{-1} \text{ K}^{-1}$.
4. The potential power of molecular mechanics thermodynamic models were illustrated by applying them to the prediction of thermodynamic equilibrium constants, $K_{eq}(T)$, for the two Diels-Alder reactions:

Our results agreed quite well with literature data for reactions (A) and (B). In addition, our computational approach required substantially less time than laboratory study (with

obvious economic benefits), and illustrated how further critique of important results is often quickly possible by carrying out additional computations for related systems.

5. The Diels-Alder dimerization of isoprene is an important reaction; dipentene (or racemic limonene), one of the products formed in this reaction, has major applications in the manufacture of polymers and adhesives. Dipentene also has various uses in the food and pharmaceutical industries. We employed the QCFF force field program to calculate gas-phase thermodynamic properties of the monomer (isoprene) and the dimers 1-methyl-5-(1-methylethenyl)cyclohexene (diprene) and 1-methyl-4-(1-methylethenyl)cyclohexene (dipentene) for the temperature range 298.15-1000K. These QCFF-calculated thermodynamic values were compared, when possible, with corresponding values obtained experimentally or from other force field programs, and the agreement was found to be satisfactory. The QCFF values were further used to derive gas-phase equilibrium properties- ΔH° , ΔS° , ΔG° , and K_p - for the isoprene dimerization reaction at various temperatures. These computational results suggested that, based upon thermodynamics, diprene and dipentene are about equally favored dimerization products of isoprene and that reported experimental data reflect kinetic control of dipentene formation at lower temperatures. This work again illustrated the power of predictive thermodynamic computational techniques in extending the thermochemical database.

6. The QCFF program originated by Warshel and Karplus was modified to compute accurate thermodynamic properties S^0 , C_p^0 , $(H_T^0 - H_0^0)/T$, and ΔH_f^0 for various acyclic and cyclic alkenes and alkadienes. Modifications consisted of adjusted bond angle, dihedral angle, bond stretch, and bond energy parameters that improved calculated vibrational frequencies, zero point energies, and thermodynamic functions. Supplemental torsional potential energy functions that were added to existing torsional functions led to greatly improved relative conformer energies and ΔH_f^0 values. In this work, it was shown that inclusion of hindered internal rotation led to significantly better agreement of calculated thermodynamic functions with observed values for acyclic alkenes at high temperatures. The calculated thermodynamic properties of the alkenes and alkadienes were deemed sufficiently accurate for calculation of standard enthalpies and Gibbs free energies of gas phase chemical reaction at various temperatures.

7. Software was written for QCPE (Quantum Chemistry Program Exchange) which calculates equilibrium conformations and vibrational normal modes of ground and PI excited states of large conjugated molecules as well as of the ground state of any other molecule (for which the potential parameters are available). The oscillator strengths of PI transitions and the I.R. intensities of the ground electronic state are also calculated. Equilibrium geometries are calculated by minimization of the molecular energy with respect to the complete set of $3N$ cartesian coordinates. The vibrational normal modes are then calculated by diagonalization of the matrix of second derivatives of the potential with respect to the mass-scaled cartesian coordinates at the calculated minimum. The efficiency of the program is based on the availability of analytical first and second derivatives of the potential with respect to the cartesian coordinates. An important feature of this program is the computation of the ideal gas entropy, the ideal gas heat

capacity, the difference of the enthalpy of the ideal gas at a given temperature from its value at zero degree K and the difference between the Gibbs free energy at a given temperature and its value at zero degree K. These thermodynamic quantities are obtained by use of the rigid rotor and harmonic oscillator models of statistical thermodynamics.

For reference see: A. Warshel and M. Karplus, J. Am. Chem. Soc., 94, 5613 (1972); S. Lifson and A. Warshel, J. Chem. Phys., 49, 5116, (1968); D. Bugay QCPE Program No. 534; S. Lifson and M. Levitt QCPE Program No. 247; T. Lenz and J. Vaughan, J. Computational Chem., 11, 351, (1990).

8. Periodic charge equilibration (PQEq) was used to study a few of the roles that the zeolite Y lattice might play in cracking catalysis. Comparison of the partial charge distributions of HY and Na₁HY suggested that atoms within 10 Å of the sodium atom accept electrons from the sodium atom. The charge distributions of *n*-octane, benzene, and water adsorbed inside the supercage of zeolite Y and siliceous zeolite Y showed that the lattice provides little perturbation to these molecules. In contrast, a local dipole in the zeolite Y lattice was found to induce a change in the partial charge distribution of a cracking hydride transfer transition state model (C₄H₉⁺ plus *n*-octane). The polarization in this transition state model was attributed to the increased size of the transition-state model in comparison to the size of *n*-octane. This polarization likely preferentially stabilizes species such as the transition state and is perhaps an explanation for the second-order dependence of hydrocarbon cracking rate on Al ion concentration in zeolite Y.

9. A molecular mechanics program (QCFF/PI) was parameterized for halogens and oxygen to compute thermodynamic functions (S° , C_p° , and $H_T^\circ - H_0^\circ$) at different temperatures. The maximum error and root mean square error between the QCFF/PI calculated heat capacities and experimental heat capacities at various temperatures for a group of alternative refrigerants were 0.28 cal/molK and 0.23 cal/molK, respectively. In addition, the effect on heats of formation for heteroatomic molecules, when incorporating the electrostatic term for atomic charges calculated using the Rappe Goddard approach also was studied. This work thus described the power of QCFF/PI in predicting the thermodynamic properties of heteroatomic molecules, among them the industrially important compounds such as alternative refrigerants.

Experimental Studies

1. Our computational-chemistry studies summarized above illustrated the power of molecular mechanics models in predicting thermodynamic properties of molecules having significant strain and structural complexity. However, there have been very few combustion calorimetric studies for bridged Diels-Alder adducts containing heteroatoms to augment the computational studies of such compounds. Thus, the adduct of anthracene and maleic anhydride: C₁₈H₁₂O₃, was measured with a model 1241 Parr automatic calorimeter and a Parr model 1710 calorimeter controller. The standard molar enthalpy of combustion of the (anthracene + maleic anhydride) adduct at $p^\circ = 0.1$ MPa was determined to be $\Delta_c H_m^\circ(\text{C}_{18}\text{H}_{12}\text{O}_3, \text{cr}, 298.15 \text{ K}) = - (8380.0 \pm 5.9 \text{ kJ} \cdot \text{mol}^{-1})$. The molar enthalpy of fusion of this adduct at its melting

temperature (534.07 K), as measured by a 910 DuPont d.s.c. and a 9900 DuPont thermal (analyzer + digital computer), was found to be $(36.3 \pm 4.2) \text{ kJ} \cdot \text{mol}^{-1}$. The other thermodynamic properties of the (anthracene + maleic anhydride) adduct derived from those measured properties were computed to be: $\Delta_f H_m^\circ(\text{C}_{18}\text{H}_{12}\text{O}_3, \text{cr}, 298.15 \text{ K}) = -(418.2 \pm 6.4) \text{ kJ} \cdot \text{mol}^{-1}$ and $\Delta_f H_m^\circ(\text{C}_{18}\text{H}_{12}\text{O}_3, \text{l}, 298.15 \text{ K}) = -(389.7 \pm 7.7) \text{ kJ} \cdot \text{mol}^{-1}$.

2. Phenylmaleic Anhydride, $\text{C}_{10}\text{H}_6\text{O}_3$, was studied by both X-ray diffraction and molecular-mechanics calculations to determine the ring-ring dihedral angle. Calculated and observed values of 5.4 and 5.53 (6)° for this dihedral angle in the crystal were found to be in good agreement; these values were quite different from the calculated value of 40° for the gas-phase structure.

Graduate Students Completing Degrees Funded Under This DOE Program

PhD Students

S. Ramachandran : Dissertation, Computer Simulation of Molecular Liquids (1994).

M. Kar : Dissertation, Predictive Chemical Thermodynamics Computations with Molecular Mechanics (1994).

Z. Buday : Dissertation, Diastereomeric Salt Formation Thermodynamics (1995).

M.S. Students

M. Kar: Dissertation, Measurement of Thermochemical and Thermophysical Properties of Structurally Complex Molecules (1990).

A. Ponamaneni: Dissertation, MM-Based Computational Thermodynamics (1995).

C. Harinarayan: Dissertation, Crystallization Studies of the Enantiomers of Lactic Acid (1996).

Publications Resulting from this work

1. Lenz, T.G.; Vaughan, J.D. *J.Phys.Chem.* **1989**, 93, 1588.
2. Lenz, T.G.; Vaughan, J.D. *J.Phys.Chem.* **1989**, 93, 1592
3. Lenz, T.G.; Vaughan, J.D. *J.Comp.Chem.* **1990**, 11, 351.
4. Lenz, T.G.; Vaughan, J.D. *Chem. Eng. Sci.* **1990**, 45, 1755.
5. Kar, M.; Lenz, T.G.; Vaughan, J.D. *J.Chem. Thermo.* **1992**, 24, 151.
6. Kar, M.; Lenz, T.G.; Vaughan, J.D. *J. Phys. Chem.* **1994**, 98, 2489.
7. Kar, M.; Lenz, T.G.; Vaughan, J.D. *J. Comp. Chem.* **1994**, 15, 1254.
8. Ponamaneni, A.K.; Lenz, T.G.; Rappe, A.K.; Vaughan, J.D. *Quantum Chem Prog. Exchange Library*, **1995**, Programs QCPE 593 and QCMP 145 and supporting documentation.
9. Ramachandran, S.; Lenz, T.G.; Skiff, W.M.; Rappé, A.K. *J. Phys. Chem.* **1996**, 100, 5898.
10. Thompson, M.A.; Kar M.; Anderson, O.P.; Lenz, T.G.; Vaughan, J.D. *Acta Crystal. Sec.C.*, **1996**, C52, 168.
11. Buday, A.; Rappé, A.K.; Lenz, T.G. *Chirality*. **1997**