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STUDY OF IMPROVED METHODS FOR PREDICTING CHEMICAL EQUILIBRIA

Terry G. Lenz
Department of Chemical Engineering

and

John D. Vaughan
Department of Chemistry

Colorado State University
Fort Collins, CO 80523

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Introduction. The objective of the research during the current and preceding periods has been to calculate thermodynamic properties (ΔH° , ΔS° , and ΔG°) of typical organic reactions in solution with sufficient accuracy to provide a viable alternative to expensive, time-consuming laboratory experimentation. The research has proceeded along five pathways. (1) Calculation of the thermodynamic properties ΔH_f° , C_p° , $(H^\circ - H_0^\circ)/T$, and S° for reactants and products in the gas phase. With these properties, one can readily calculate reaction thermodynamic properties, including equilibrium constants, for gas phase reactions at a variety of temperatures. During past periods, we used existing molecular mechanics (MM) programs to calculate equilibrium constants over wide temperature ranges for the Diels-Alder dimerizations of 1,3-cyclopentadiene¹ and butadiene², respectively, and the Diels-Alder condensations of cyclopentadiene with acetylene and ethylene³, respectively, and of butadiene with ethylene²; in all instances the calculated equilibrium constants exhibited excellent agreement with experimental values. Since these molecular mechanics programs, MOLBD3^{1,3,4} and combined MMP2⁵ and QCFF/PI⁶ have distinct limitations in the accuracy and general applicability of their calculations, we are currently transforming QCFF/PI into a general thermodynamic program that can generate ΔH_f° , C_p° , $(H^\circ - H_0^\circ)/T$, and S° for saturated and unsaturated hydrocarbons, aromatics, and heteroatomic organics. (2) Transformation of gas phase thermodynamic properties of reactants and products into condensed phase properties by use of observed vapor pressure data. (3) Experimental determination of X-ray crystal structures, vapor and sublimation pressures, and calorimetric standard enthalpies of formation of large, relatively complicated reactants and products, such as Diels-Alder adducts of substituted anthracenes and substituted maleic anhydrides. These experimental data, not available in the literature, provide necessary support for the computational procedures emerging from pathways (1) and (2). (4) Experimental determination of equilibrium constants of Diels-Alder reactions of complicated, strained dienes and dienophiles over a range of temperatures in liquid solution. These data, coupled with vapor or sublimation pressure data, provide definitive tests for molecular mechanics calculations of gas phase equilibrium properties. (5) Molecular dynamics

study of pure liquids and liquid mixtures to eventually permit new activity coefficient models being developed. Given activity coefficients, one can calculate equilibrium concentrations from the calculated equilibrium constants.

Progress during the period 7/1/89 to 8/31/90 was made in three areas:

- A. Modification of QCFF/PI.
- B. Experimental Calorimetric, Vapor Pressure, Sublimation Pressure, and X-ray Structure Determination.
- C. Liquid Phase Molecular Dynamics Modeling.

A. Modification of QCFF/PI.

A specific goal in the development of our thermodynamic molecular mechanics (MM) program from QCFF/PI is to incorporate the following required characteristics. (1) Large force field parameter base, that will permit calculations of thermodynamic properties and structural parameters for a wide range of saturated, unsaturated, aromatic, and heteroatomic organic molecules. (2) Dihedral drive routine, that will carry out stepwise rotations of atomic coordinates around a chosen bond, thereby locating maxima and minima in the torsional potential energy function of the bond. Hence, conformers (rotomers) are located, the energy of each computed, and barriers to internal rotations determined. (3) Subprogram that calculates the product of principal moments of inertia (for external rotation) and reduced moments of inertia (for internal rotations). (4) Subprogram that calculates hindered internal rotational contributions to the molecular energy and the thermodynamic functions. (5) A base of transferable bond energy parameters, which when combined with zero point energy, molecular energy, elemental atomization energies, and $(H^\circ - H^\circ_0)$, yield reliable ΔH°_f predictions.

A dihedral driver subprogram was written into QCFF/PI during the current period. This addition, together with the introduction of modified linear torsional terms, resulted in significantly improved energy differences of conformers, barriers to internal rotation, and torsional contributions to molecular energy, zero point energy, and the thermodynamic functions. Because

of these changes, it has become necessary to adjust bond energy parameters worked out in earlier periods commensurately. Although these adjustments are still in progress, the results to date are encouraging. The adjusted bond energy parameters exhibit greater transferability than before, so that deviations of calculated ΔH_f° for compounds from observed values is lessened.

Considerable progress has been made in our goal to include hindered internal rotational contributions into the main program. Generally, these contributions are small, but can become significant for hindered internal rotation around single bonds at high temperature and for bonds with small barriers to internal rotation (for example, biphenyl). Although procedural details have been worked out, we have not completed the necessary software changes at this time.

A limitation that affects MM programs in general is the accuracy of experimental thermodynamic and structural data for prototypic molecules that are used to calibrate the programs. This consideration becomes increasingly important as MM programs become more sophisticated and capable of greater precision and accuracy. The point is illustrated by 1,3-butadiene, which along with benzene and ethylene, is used in parameter determinations in MM programs that treat conjugated pi systems. At temperatures below 425 K, thermodynamic properties determined calorimetrically⁷ for mixture of s-trans and s-cis forms are generally accepted to be accurate, but the mole fractions of the mixtures, based on early spectral data⁸ are not, and therefore the thermodynamic properties of the s-trans and s-cis forms are not accurate. We have updated ΔH_f° , C_p° , $(H^\circ - H_0^\circ)/T$, and S° for the s-trans and s-cis conformers over a wide temperature range (200 K to 1200 K) using the latest spectral assignments^{9,10}, structural parameters^{11,12}, and torsional potential energy functions^{13,14}. A manuscript covering this updated thermodynamic data is presently being prepared for submission this fall.

B. Experimental Calorimetric, Vapor Pressure, Sublimation Pressure, and X-ray Structural Determination.

1. Calorimetric Determinations. Standard enthalpies of formation of three Diels-Alder adducts were determined by combustion in a Parr model 1241 automatic adiabatic calorimeter. Two of the

compounds combusted were liquids, 4-methylcyclohexene and 4-vinylcyclohexene (adducts of 1,3-butadiene and propene and of 1,3-butadiene dimerization, respectively) and the third was the crystalline adduct of anthracene and maleic anhydride. In addition, the standard enthalpy of fusion of the latter adduct was determined by differential scanning calorimetry. The above experimental investigations are described in detail in two papers recently submitted^{15,16}.

2. Vapor Pressure. Vapor pressure as a function of temperature was determined for 4-methylcyclohexene and 4-vinylcyclohexene by the boiling-point method; linear plots of $\ln P$ vs. T^{-1} were obtained. Standard enthalpies of vaporization were determined from the vaporization data, which together with the standard enthalpies of formation of the liquids, yielded standard enthalpies of formation of the gaseous compounds. Experimental details and results are given in reference 15.

3. Sublimation Pressure. A high-vacuum system designed specifically for Knudsen sublimation pressure measurement has been assembled and is nearly ready for operation. Our purpose is to determine sublimation pressures of solid-phase diene, dienophile, and Diels-Alder adducts at various temperatures, from which data one can transform standard enthalpies of formation of solids to corresponding values for the gas phase.

4. X-ray Structure. Detailed X-ray crystallographic studies have been completed on the dienophile 3-phenylmaleic anhydride and the adducts anthracene/maleic anhydride, anthracene/3-phenylmaleic anhydride, and 9-phenylanthracene/maleic anhydride. The X-ray study of the diene 9-phenylanthracene remains to be done.

5. Molecular Dynamics Simulations. A molecular dynamics program is being written which will permit study of pure solid, liquid or gas species in the N, P, T ensemble.

References.

1. T. G. Lenz and J. D. Vaughan, *J. Phys. Chem.* **1989**, *93*, 1592.
2. T. G. Lenz and J. D. Vaughan, *J. Comput. Chem.* **1990**, *11*, 351.
3. T. G. Lenz and J. D. Vaughan, *Chem. Eng. Sci.* **1990**, *45*, 1755.

4. S. Chang, D. McNally, S. Shary-Tehrany, M. Hickey, and R. H. Boyd, *J. Am. Chem. Soc.* **1970**, 92, 3109.
5. N. L. Allinger and H. L. Flanagan, *J. Comput. Chem.* **1983**, 4, 399.
6. A. Warshel and M. Karplus, *J. Am. Chem. Soc.* **1972**, 94, 5612.
7. R. B. Scott, C. H. Meyers, R. D. Rands, F. G. Brickwedde, and N. Bakkedahl, *J. Res. N.B.S.*, **1945**, 35, 39.
8. J. G. Aston, G. Szasz, H. L. Wooley, and F. G. Brickwedde, *J. Chem. Phys.* **1946**, 14, 67.
9. R. K. Harris, *Spectrochim. Acta.* **1964**, 20, 1129.
10. Y. N. Panchenko, *Spectrochim. Acta.* **1975**, 31, 1201.
11. W. Haugen and M. Traetteberg, *Acta. Chem. Scand.* **1966**, 20, 1726.
12. K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Molec. Struct.* **1967**, 1, 463.
13. L. A. Carrier, *J. Chem. Phys.* **1975**, 62, 3857.
14. C. W. Book, P. George, M. Trachtman, and M. Zanger, *J.C.S. Perkin II* **1979**, 26.
15. M. Kar, T. G. Lenz, and J. D. Vaughan, *J. Chem. Eng. Data*, submitted, June, 1990.
16. M. Kar, T. G. Lenz, and J. D. Vaughan, *J. Chem. Thermodynamics*, submitted, May, 1990.

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