HEATS OF HYDROGENATION

Experimental and
Computational Hydrogen
Thermochemistry of
Organic Compounds

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Dedicated to the memory of Frank McLafferty
Scholar, Teacher, Friend

He maketh me to lie down in green pastures...

Psalms 23

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Preface

Hydrogen thermochemistry consists of obtaining useful thermodynamic information by measuring the heat output upon adding hydrogen across the double or triple bond or bonds of an unsaturated organic molecule. Though far less general in its application than combustion thermochemistry, it is simpler and it produces results of comparable accuracy. Heats of hydrogenation constitute a body of thermochemical information that has had a historical significance far out of proportion to the small number of research groups that have engaged in the work. Early studies (1935–1939) by Kistiakowski and coworkers at Harvard produced some of the most widely quoted results in all of thermochemistry, among them the conjugation energy of 1,3-butadiene and the resonance energy of benzene. After an initial, highly productive period, however, hydrogen thermochemistry was cut short by World War II, and it languished until the late 1950s, largely because chemists favored the vastly more general competing method of oxygen bomb calorimetry.

Recent highly accurate quantum mechanical calculations requiring reference standards of comparable accuracy and the economics of fuels and petrochemicals have brought hydrogen thermochemistry back into contemporary focus. There is at present no critical survey of the scattered literature on experimental methods and results of hydrogen thermochemistry, or the burgeoning field of computational hydrogen thermochemistry. This short monograph is intended to fill that gap. It is divided into three chapters, each covering a distinct part of hydrogen thermochemistry:

1. Practical and historical aspects of experimental determination of the enthalpies of hydrogenation and formation $\Delta_{\text{hyd}}H_{298}$ and $\Delta_f H_{298}$ of organic compounds, primarily hydrocarbons, are given in Chapter 1.
2. Chapter 2 consists of a large table containing more than 500 $\Delta_{\text{hyd}}H_{298}$ values measured over 70 years of research, now scattered throughout the literature in English and in German. One of the unusual aspects of this literature is that contemporary experimental advances, though they have brought about an increase in sensitivity measured in orders of magnitude, they have not brought about a significant change in accuracy. Thus the older literature contains results that are as valuable today as they were when they were first published. Like all literatures, however, the hydrogen thermochemical literature varies in accuracy and reliability, both of which are commented upon within this table.
3. Contemporary advances in computer hardware and software have brought about a immense increase in our ability to calculate (as distinct from measuring) $\Delta_{\text{hyd}}H_{298}$. Modern computational thermochemistry includes various empirical, semiempirical, and quantum mechanical methods for calculating $\Delta_{\text{hyd}}H_{298}$ of linear and cyclic alkenes, polyalkenes, alkynes and polyalkynes. There is at present no critical survey of computational methods for determining $\Delta_{\text{hyd}}H_{298}$ which Chapter 3 supplies.

Whatever technological problems and successes the future may bring, we can be assured that they will be within the framework of classical thermodynamics.

The author wishes to acknowledge the help and encouragement of colleagues and friends Joel Liebman, Nikita Matsunaga, and Andreas Zavitsas. As always, I express my thanks to Tony Zeru Li for extracting me from the computational problems I have created for myself in writing this book.

Greenwich Village NY

Donald W. Rogers

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