IUPAC Project 2003-024-1-100
Thermochemistry of Free Radicals and Critical Intermediates of Importance to Combustion and the Atmosphere: Properties from Theory and Experiment

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Central project objective: The principal objective is to critically evaluate thermodynamic properties of chemical species that are relevant in combustion and atmospheric chemistry. The recommended enthalpies of formation are based on *all available experimental and theoretical data*, complemented by additional state-of-the-art electronic structure calculations.

The relevant experimental data are collected from published spectroscopic, kinetic, and ion chemistry measurements, and are recomputed and reinterpreted in light of the latest knowledge. Existing high-level theoretical computations from the literature are also included, and additional computations are systematically performed at various levels of theory.

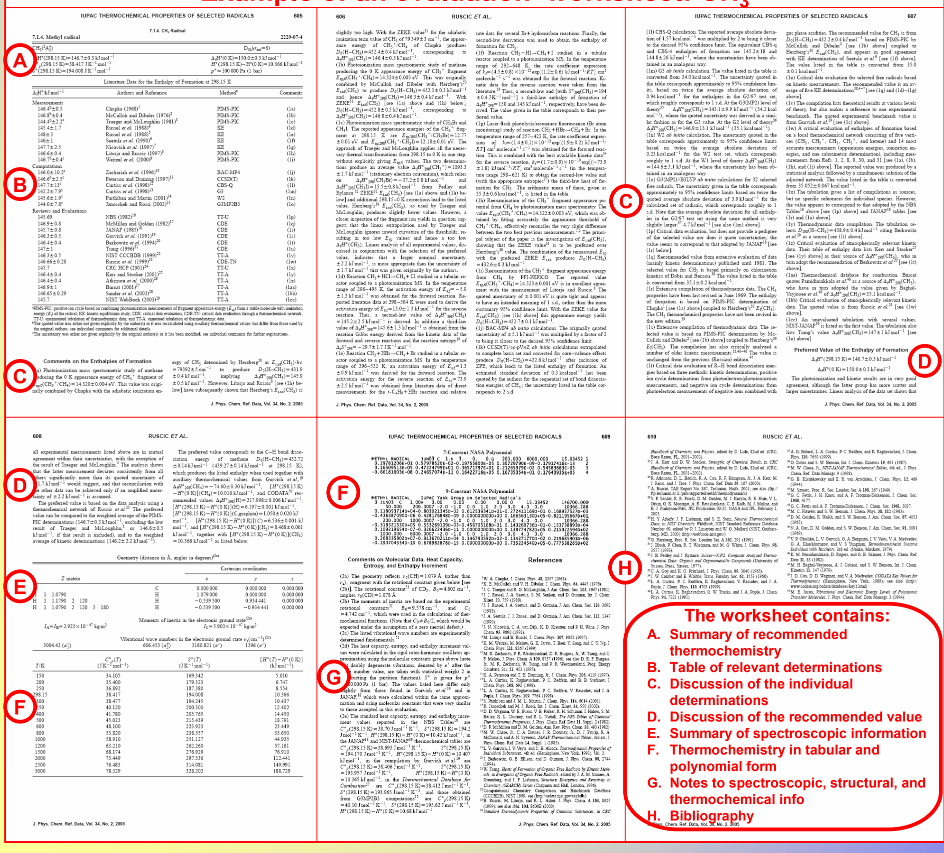
The critical evaluation process: The TG membership is roughly equally split between experimentalists and theorists. Target lists of radicals are compiled based on critical needs for reliable thermochemistry in combustion and atmospheric kinetics and modeling, and draws on the combined expertise of the TG members and input from outside the TG. For example, "Set 1" originally contained 32 radicals, and "Set 2" contained 60 radicals; both have been recently additionally expanded. For each of the target species, a worksheet is compiled. The initial information on the worksheets is comprised of a set of individual entries, each of which is based on one of the available experimental and theoretical determinations from the literature. Each entry is individually critically evaluated as per scientific soundness, objective merit and reliability, and, if appropriate, reinterpreted and/or recomputed from the original measurement. In parallel to this activity, G3B3(MP2) computations are systematically and uniformly performed for all target species. In most cases, the target species are additionally examined using the highest applicable theoretical treatments, such as W4, W3, W2, and Focal-Point, augmenting the knowledge base itemized in the worksheet. When all thermochemically-relevant determinations for one target species are evaluated and entered into the worksheet, a second round of critical evaluations is performed, where the individual entries are compared in multiple manners and statistically analyzed for cross-consistency, uncovering hidden systematic errors, etc. The technology employed for the statistical evaluation and the internal consistency tests is based on the recently developed Active Thermochemical Tables approach. Depending on the outcome, the final evaluation process either leads to the recommended values, or indicates that the evaluation process needs to be reiterated or that additional high-level theoretical computations or new experiments would be highly desirable.

Progress: A substantial part of the work has been completed and 35 papers have so far appeared or are in press (with another 8 papers from the predecessor Project 2000-013-1-100 concluded at the end of 2003). Additional papers are being written as the work progresses.

While the central goal of this project is to perform a systematic critical thermochemical evaluation of radicals and other species relevant in combustion and the atmosphere, the scientific problems that are being uncovered and formulated during the evaluation have become a unique *spiritus movens* that is motivating ground-breaking research and development of new general methods (within the regular research grants of the TG members and involving broader collaborative efforts). This is especially the case in the areas of dealing efficiently with complex interrelationships inherently present in thermochemistry (Active Thermochemical Tables, ATcT) and developing new state-of-the-art electronic structure calculations (W3, W4, HEAT, and HEAT II).

This project also served as a pilot user of the recently completed Collaboratory for Multi-Scale Chemical Science (CMCS, see: http://cmcs.org, funded through the U.S. Department of Energy SciDAC initiative), thus pioneering the use of advanced web-based collaborative and data management technologies in IUPAC Projects.

Example of an evaluation worksheet: CH_3



Partial selection of recent publications related to this project (see http://www.iupac.org/projects/2003/2003-024-1-100.html for a longer list):

- ***IUPAC Critical Evaluation of Thermochemical Properties of Selected Radicals: Part I.***
  B. Ruscic, J. E. Boggs, A. Burcat, A. G. Császár, J. Demaison, R. Janoschek, J. M. L. Martin, M. L. Morton, M. J. Rossi, J. F. Stanton, P. G. Szalay, P. R. Westmoreland, F. Zabel, and T. Bérces
  ***J. Phys. Chem. Ref. Data* 34, 573-656 (2005)**
- *Unimolecular Thermal Fragmentation of ortho-Benzyne*
  X. Zhang, A. T. Maccarone, M. R. Nimlos, S. Kato, V. M. Bierbaum, B. K. Carpenter, G. B. Ellison, B. Ruscic, A. C. Simmonett, W. D. Allen, and H. F. Schaefer III, *J. Chem. Phys.* **126**, 044312 (2007)
- *W4 Theory for Computational Thermochemistry: In Pursuit of Confident sub-kJ/mol Predictions*
  A. Karton, E. Rabinovich, J. M. L. Martin, and B. Ruscic, *J. Chem. Phys.* **125**, 144108 (2006)
- *High-accuracy Extrapolated ab initio Thermochemistry. II. Minor Improvements to the Protocol and a Vital Simplification*
  Y. J. Bomble, J. Vazquez, M. Kallay, C. Michauk, P. G. Szalay, A. G. Csaszar, J. Gauss, and J. F. Stanton, *J. Chem. Phys.* **125**, 064108 (2006)
- *The Origin of Systematic Error in the Standard Enthalpies of Formation of Hydrocarbons Computed via Atomization Schemes*
  G. Tasi, R. Izsak, G. Matisz, A. G. Csaszar, M. Kallay, B. Ruscic, and J. F. Stanton, *Chem. Phys. Chem.* **7**, 1664 (2006)
- *Active Thermochemical Tables: Accurate Enthalpy of Formation of Hydroperoxyl Radical, HO_2*
  B. Ruscic, R. E. Pinzon, M. L. Morton, N. K. Srinivasan, M.-C. Su, J. W. Sutherland, and J. V. Michael, *J. Phys. Chem. A* **110**, 6592 (2006)
- *The Molecular Structure, Spin-vibronic Energy Levels, and Thermochemistry of CH_3O*
  A. V. Marenich and J. E. Boggs, *J. Mol. Struct.* **780**/**781**, 163 (2006)
- *Enthalpies of Formation of Small Free Radicals and Stable Intermediates: Interplay of Experimental and Theoretical Values*
  R. Janoschek and W. M. F. Fabian, *J. Mol Struct.* **780**/**781**, 80 (2006)
- *Accurate ab initio Determination of Spectroscopic and Thermochemical Properties of Mono- and Dichlorocarbenes*
  G. Tarczay, T. A. Miller, G. Czakó, and A. G. Császár, *Phys. Chem. Chem. Phys.* **7**, 2881 (2005)
- *Thermochemical Properties of the Hydroxy-formyl Radical HOCO, and the Formyloxy Radical, HC(O)O, and their Role in the Reaction OH + CO → H + CO2: Computational G3MP2B3 and CCSD(T)-CBS Studies.*
  W. M. F. Fabian and R. Janoschek. *TheoChem* **713**, 227 (2005)
- *Ab Initio Determination of the Heat of Formation of Ketenyl (HCCO) and Ethynyl (CCH) Radicals*
  P. G. Szalay, A. Tajti, and J. F. Stanton, *Mol. Phys.* **103**, 2159 (2005)
- *Third Millennium Ideal Gas and Condensed Phase Thermochemical Database for Combustion with Updates from Active Thermochemical Tables*
  A. Burcat and B. Ruscic, Joint Report ANL-05/20, Argonne National Laboratory, Argonne, IL, USA, and TAE 960, Technion – Israel Institute of Technology, Haifa, Israel (2005)
- *Thermochemical Properties of Free Radicals from G3MP2B3 Calculations, Set-2: Free Radicals with Special Consideration of CH_2=CH-C=CH_2, cyclo-C_5H_5, CH_2OOH, HO-CO, and HC(O)O.*
  R. Janoschek and M. J. Rossi. *Int. J. Chem. Kinet.* **36**, 661 (2004)

Acknowledgment of funding sources: The members of this Task Group wish to express their appreciation to IUPAC for the financial support which facilitated and accelerated the progress on this project. However, in a project of such a large scope, various related activities of the TG members have been by necessity supported from their individual research grants. Hence, this project has benefited from partial support by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences under Contracts No. DE-AC02-06CH11357 (B. R., Argonne National Laboratory) and DE-FG02-91ER14192 (P. R. W., U. of Massachusetts Amherst), the U.S. Department of Energy, Office of Advanced Scientific Computing Research, Division of Mathematical, Information and Computational Science under various contracts (CMCS), the Hungarian Science Foundation Project Nos. T043601, T037690 (T.B.),T033074 (A. G. Cs.), and T032980 (P. G. Sz.), the Swiss National Science Foundation (M. J. R.), the Office Federal de l'Enseignement et de la Science (M. J. R.), and the Lise Meitner-Minerva Center for Computational Quantum Chemistry (J. M. L. M.)