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

Branko Ruscic (*Chair*),[a] Tibor Bérces, (*Chair Emeritus*),[b] James E. Boggs,[c] Alexander Burcat,[d] Attila Császár,[e] Jean Demaison,[f] Rudolf Janoschek,[g] Jan M. L. Martin,[h] Michel J. Rossi,[i] John Stanton,[c] Péter Szalay,[e] Phillip R. Westmoreland,[j] and Friedhelm Zabel[k]

[a] Chemistry Division, Argonne National Laboratory, Argonne, IL, USA; [b] Hungarian Academy of Sciences, Institute of Chemistry, Chemical Research Center, Budapest, Hungary; [c] Department of Chemistry, University of Texas, Austin, TX, USA; [d] Faculty of Aerospace Engineering, Technion - Israel Institute of Technology, Haifa, Israel; [e] Department of Theoretical Chemistry, Lorand Eötvös University, Budapest, Hungary; [f] Laboratoire de Physique des Lasers, Atomes et Molecules, Universite de Lille, Villeneuve d'Ascq, France; [g] Institut für Theoretische Chemie, Karl-Franzens-Universität Graz, Graz, Austria; [h] Department of Organic Chemistry, Weizmann Institute of Science, Rechovot, Israel; [i] LPA-Laboratoire de Pollution Atmosphérique, ISTE-Institut des Sciences et Technologies de l'Environnement, EPFL-Ecole Polytechnique Fédérale de Lausanne, Lausanne, Switzerland; [j] Department of Chemical Engineering, University of Massachusetts Amherst, Amherst, MA, USA; [k] Institut für Physikalische Chemie, Stuttgart Universität, Stuttgart, Germany

Central project objective: The principal objective is to provide critically evaluated 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 in most cases recomputed or 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.

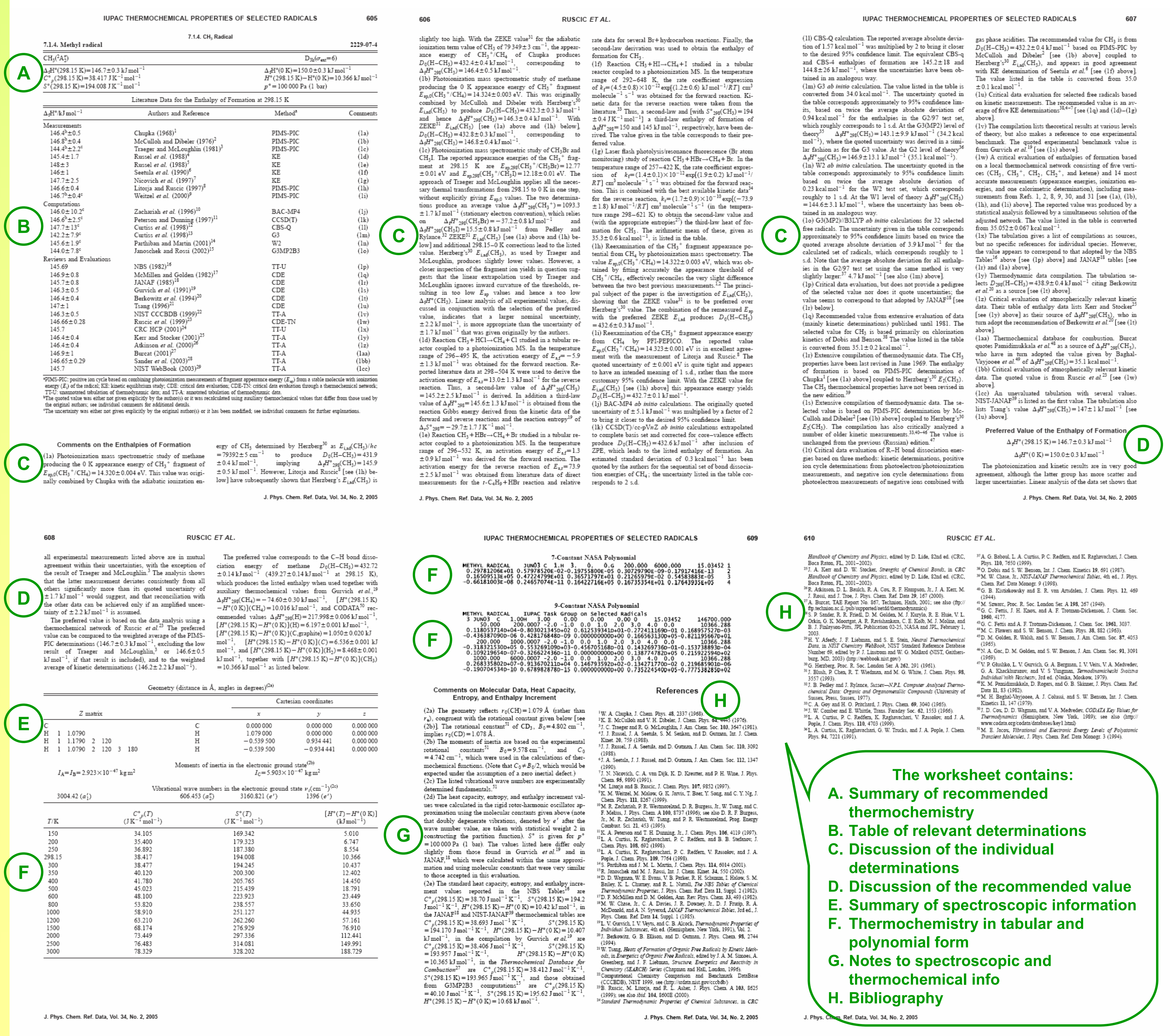
The critical evaluation process: The TG membership is roughly equally split between experimentalists and theorists. Target lists of radicals are compiled based on critical needs for reliable thermochemistry in combustion and atmospheric kinetics and modeling, and draws on the combined expertise of the TG members and input from otside the TG. For example, “Set 1” contained originally 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 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 13 papers have appeared or are in press during 2004-05 (and 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 and HEAT).

This project has also become a pilot user of the recently developed 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 list of recent publications related to this project (see also 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)**

• *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)

•*W3 Theory: Robust Computational Thermochemistry in the kJ/mol Accuracy Range.*
A. D. Boese, M. Oren, O. Atasoylu, and J. M. L. Martin. *J. Chem. Phys*. **120**, 4129 (2004)

• *HEAT: High Accuracy Extrapolated Ab Initio Thermochemistry.*
A. Tajti, P. G. Szalay, A. G. Császár, M. Kállay, J. Gauss, E. F. Valeev, B. A. Flowers, J. Vázquez, and J. F. Stanton. *J. Chem. Phys*. **121**, 11599 (2004)

• *Benchmark Thermochemistry of the Hydroperoxyl Radical.*
B. A. Flowers, P. G. Szalay, J. F. Stanton, M. Kállay, J. Gauss, and A. G. Császár. *J. Phys. Chem. A* **108**, 3195 (2004)

• *Introduction to Active Thermochemical Tables: Several “Key” Enthalpies of Formation Revisited.*
B. Ruscic, R. E. Pinzon, M. L. Morton, G. Von Laszevski, S. J. Bittner, S. G. Nijsure, K. A. Amin, M. Minkoff, and A. F. Wagner.
J. Phys. Chem. A **108**, 9979 (2004)

•*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. *J. Mol. Struct. TheoChem* **713**, 227 (2005)

•*Vibrational Spectrum and Thermochemistry of the Formyl (HCO) Radical: A Variational Study by the Coupled Cluster CCSD(T) Method with Complete Basis Set Extrapolation.*
A. V. Marenich and J. E. Boggs. *J. Phys. Chem. A* **108**, 5431 (2004)

• *Thermodynamic Properties of C1 and C2 Bromo Compounds and Radicals: A Relativistic ab Initio Study.*
M. Oren, M. A. Iron, A. Burcat, and J. M. L. Martin. *J. Phys. Chem. A* **108**, 7752 (2004)

•*Active Thermochemical Tables*
B. Ruscic, in: 2005 Yearbook of Science and Technology, McGraw-Hill, New York, 2004, pp. 3-7

• *Equilibrium Geometry of the Ethynyl (CCH) Radical.*
P. G. Szalay, L. S. Thøgersen, J. Olsen, M. Kállay, and J. Gauss. *J. Phys. Chem. A* **108**, 3030 (2004)

• Pulsed Field Ionization Photoelectron-photoion Coincidence Study of the Process $N_2 + h\nu \rightarrow N^+ + N + e^-$: Bond Dissociation Energies of N_2 and N_2^+
X. Tang, Y. Hou, C. Y. Ng, and B. Ruscic.
J. Chem. Phys. 123, xxx (2005) *in press*

• *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**, xxx (2005) *in press*

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