Thermochemistry Standards

The *Chemistry Webbook* of the National Institute of Standards (NIST) in the United States is basically the internet version of the "yellow book", a thorough and almost comprehensive compilation of experimental thermochemical data for gaseous neutral and ionic compounds.[1] The most recent release (2001) of the internet version covers more than 40 000 species. However, only few organometallic species are included, and for more specialized searches consultation of the recent review by Ervin[2] is recommended.

The design of the *webbook* is simple and clear. Fancy and data-transfer demanding items seem to be omitted deliberately. The user interface offers rapid access to remarkably efficient search algorithms. While the molecular formula is probably the major search item, properties can also be searched, such as ionization energies, electron affinities, and molecular masses, but also CAS numbers, trivial names and others. Simple structural formulae may also be drawn and submitted. Some options are of limited use, however, because not all species included in the database can be classified in these terms, such as van der Waals complexes. Once you have chosen a search method, you are asked for the search item and the properties of interest. If more than a single species is contained in the database, the available species are listed; another click leads to the data of interest. The data range from condensed phase properties to ion energetics; more than 10 000 mass spectra are available. Each property is listed along with a link to the complete reference. Moreover, the full set of data is cross-linked so that all substances examined in a particular publication can be displayed (except databases, however).

As an example, let us search for fulvene. Entering C_6H_6 in formula search mode leads to a list of sixteen isomers. To include ions, check the adequate box. Scrolling the list leads to fulvene for which name, formula, and structure are given. Upon selection, the experimental data available for this molecule are displayed (Figure 1), which include the heat of formation, the boiling point, the heat of hydrogenation, and the ionization energy.

Despite the admiration, there are some aspects to criticize. Thus, the data for some compounds are inconsistent. For example, the webbook quotes two values for the heat of formation of difluorocarbene. The previous value[1] is not listed, and no reason for the actual choice is given. Theory even indicates that the values quoted in the webbook are somewhat too large, and supports the previous value.[3] Updating is another, but understandable drawback. For example, the heat of formation of the phenyl radical still quotes an older value though a more precise one is available.[4] Error report forms are found on each page, and I sent several of those in the last years, but never received any feedback. Minor items concern the lack of error margins and heats of formation at 0 K in many cases, inconsistent nomenclature (for example 1,2- and 1,3-dimethylbenzene, but *p*-xylene for the 1,4-isomer), and wrong structures (the entry for thioacetone shows the formula of thiopropanal).

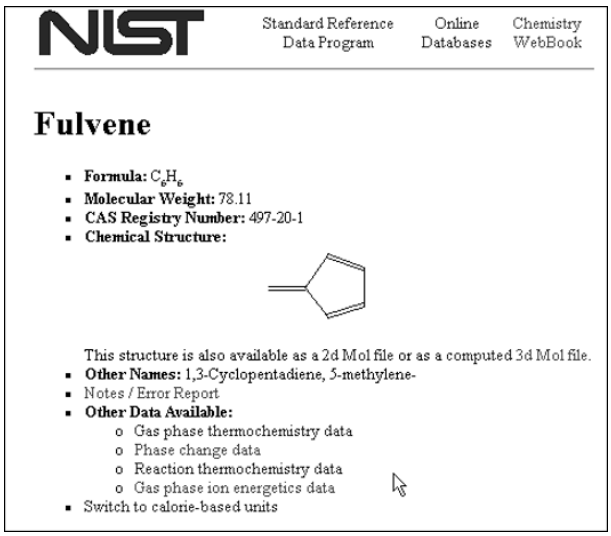

Figure 1. Fulvene data in the Chemistry Webbook.

In summary, the webbook provides a user-friendly, rational access to a huge database which is of great value for all kinds of thermodynamic considerations. Like any compilation of data, however, the quoted values are neither free of typos nor systematic errors. For example, when several groups reported systematically "wrong" values for a certain compound, a single experiment which gives the "correct" value might be discarded in the process of data evaluation. Of course, one cannot blame the NIST for such entries, but consultation of the original sources is strongly recommended whenever serious mismatches occur.

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[1] S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallard, *J. Phys. Chem. Ref. Data* **1988,** *17*, Suppl. 1.
[2] K. Ervin, *Chem. Rev.* **2001**, *101*, 391.
[3] A. Ricca *J. Phys. Chem. A* **1999**, *103*, 1878.
[4] G. E. Davico, V. M. Bierbaum, C. H. DePuy, G. B. Ellison, R. R. Squires *J. Am. Chem. Soc.* **1995**, *117*, 2590.

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