

# Molecular Thermochemistry: 20 Years of Experiments and Estimates

## Termodinâmica Molecular: 20 Anos de Experiências e Estimativas

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The present paper provides a brief overview of Molecular Thermochemistry research made at Lisbon, throughout two decades. Those experimental studies, which have been concerned with the energetics of many organometallic, organic, and inorganic substances, led to the development of methods to estimate new data. A few recent examples, including  $\beta$ -elimination and DNA-repair reactions, and the bonding in alkaline metal alkoxides and fullerenes, were selected to illustrate the energetics-structure-reactivity relationship.

### 1. Is Molecular Thermochemistry old-fashioned?

Molecular Thermochemistry aims to investigate the stability of individual molecules. *Stability* is, however, a fairly ambiguous concept. A water molecule, which meets our intuitive criteria of endurance, is promptly destroyed in the presence of sodium atoms. Methane, with its four strong carbon-hydrogen bonds, is easily consumed by reaction with oxygen. Hydrogen peroxide, having a rather weak oxygen-oxygen bond, may survive forever under appropriate conditions. Therefore, a given molecule exists only under certain physical and chemical environments. And when it is said to be *stable*, one should ask: "Stable, relative to what?"

Thermodynamics provides the tools to analyze the type of stability mentioned above, known as *thermodynamic stability*. For instance, the yield of a chemical reaction in the gas phase, at a given temperature and pressure, can be calculated from the equilibrium constant ( $K$ ), which is related to the standard Gibbs energy of that reaction.

Apresenta-se, neste artigo, uma breve panorâmica dos estudos sobre Termodinâmica Molecular realizados em Lisboa, nos últimos vinte anos. O trabalho experimental, que envolveu uma variedade de compostos organometálicos, orgânicos e inorgânicos, conduziu também ao desenvolvimento de métodos de estimativa de novos dados termodinâmicos. Com o objectivo de ilustrar a relação entre energética, estrutura e reactividade moleculares, são apresentados alguns exemplos recentes, incluindo reacções de eliminação  $\beta$  e de reparação do ADN, bem como a investigação da natureza das ligações químicas em fullerenos e em alcóxidos de metais alcalinos.

As indicated by the familiar equation 1,  $\Delta_r G_m^\circ$  can be obtained from the standard enthalpy and entropy of the reaction.  $\Delta_r H_m^\circ$  and  $\Delta_r S_m^\circ$  can in turn be derived from the standard enthalpies of formation and the standard entropies of reactants and products [1].

$$-RT \ln K = \Delta_r G_m^\circ = \Delta_r H_m^\circ - T\Delta_r S_m^\circ \quad (1)$$

A reaction Gibbs energy is therefore a measure of the thermodynamic stability of a given molecule, under given chemical and physical conditions. However, at room temperature, the term  $T\Delta_r S_r^\circ$  is often small compared to  $\Delta_r H_m^\circ$ , implying that the reaction enthalpy is the dominant term in equation 1. As  $\Delta_r H_m^\circ$  is calculated from the standard enthalpies of formation, these quantities can thus be regarded as gauges of thermodynamic stability.

A large number of Molecular Thermochemistry studies have been concerned with the thermodynamic stability of chemical bonds rather than with the thermodynamic stability of molecules as a whole. Both types of information - bond dissociation enthalpies

(see Appendix) and enthalpies of formation, respectively - enable the calculation of reaction enthalpies. In many occasions, however, the former are the only data available. Consider, for instance, vitamin E ( $\alpha$ -tocopherol, TcOH; see Figure 1), which breaks the lipid peroxidation cycle by reacting with a lipid peroxy radical ( $\text{ROO}^\bullet$ ) [2]. Although the enthalpies of formation of reactants and products are unknown, the enthalpy of reaction 2 can be calculated from equation 3 because the enthalpies of the bonds cleaved and formed are accessible.



$$\Delta_r H_m^\circ(2) = DH_{\text{sln}}^\circ(\text{TcO}-\text{H}) - DH_{\text{sln}}^\circ(\text{ROO}-\text{H}) \quad (3)$$

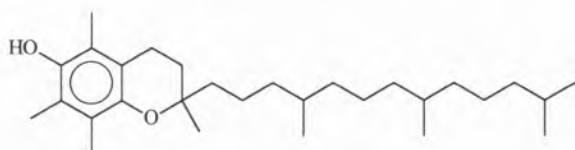


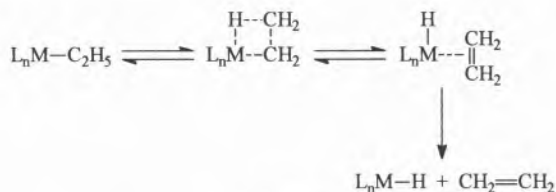
Figure 1 – Chemical structure of  $\alpha$ -tocopherol.

The importance of bond dissociation enthalpies is not confined to the calculation of reaction enthalpies. They may also lead to insights into reaction kinetics and mechanisms. For example, Ingold and coworkers have found a correlation between the O–H bond dissociation enthalpies of several substituted phenols and the respective rate constants of the hydrogen abstraction reactions by peroxy radicals [3]. The low O–H bond dissociation enthalpy in vitamin E is consistent with a high rate constant of reaction 2 and is in keeping with the good antioxidant properties of this substance.

A general treatment of the fascinating bridges between thermochemistry and kinetics is included in a famous book by Benson [4]. Unfortunately, the relationships are not always as simple as in the case of substituted phenols. It is often found that the *kinetic stabilities* of molecules belonging to a given family do not correlate with their thermodynamic stabilities. The former, being determined by the reaction mechanism, depend on the size of the activation barrier and on other details of the reaction profiles; the latter are simply determined by the thermodynamics of reactants and products. In other words, the instability of a molecule can have a “purely” kinetic origin.

The distinction between thermodynamic and kinetic stability of a compound or a chemical bond was the driving force to start the thermochemical studies in Lisbon, some 20 years ago. The groups of Wilkinson and Lappert had noted that the instability of some transition metal compounds containing metal-carbon bonds could have a kinetic root [5,6] and would not necessarily imply that those bonds were weak. It had been

recognized, for example, that a metal complex  $\text{M}(\text{L})^n(\text{C}_2\text{H}_5)$ , where L represents a ligand like phosphine, cyclopentadienyl, etc., decomposes through a mechanism known as  $\beta$ -elimination. As observed in Scheme 1, the destabilization of the four-centered transition state, due to the stretching of the metal-carbon bond, is compensated by the formation of an incipient metal-hydrogen bond. The pathway does not require the simple cleavage of the M–C  $\sigma$  bond. Hence, the thermodynamic stability cannot be inferred from the decomposition temperature of the compound.



Scheme 1

In 1975, the controversy around the stability of transition metal-alkyl complexes stimulated the interest of Romão Dias, head of the Organometallic Chemistry group at IST, and Calado, head of the Experimental Thermodynamics group at the same Institute. One of the outcomes of joint discussions was the decision to hire a graduate student to work on the project. Another was to use some form of calorimetry to investigate the problem. As this technique was not in their area of expertise, in order to proceed more rapidly some outside help was sought. Two groups (from the University of Manchester, UK, and University of Porto, Portugal) gave a very significant contribution during the first steps. The British group (Skinner, Pilcher and Connor [7]) was the leading authority on thermochemistry of organometallic compounds and used several types of calorimetry, particularly Calvet (heat-flux) microcalorimetry. The interests of the Portuguese group, headed by Ribeiro da Silva, were in thermochemistry of coordination complexes. The main technique used in their studies was isoperibol reaction-solution calorimetry. To make a long story short, after an undetermined number of attempts to probe the thermochemistry of some molybdenum and tungsten bis( $\eta^5$ -cyclopentadienyl) complexes,  $\text{M}(\text{Cp})_2\text{L}_2$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{L} = \text{H}, \text{Me}$ ), anaerobic reaction-solution calorimetry (RSC) was finally recognized as the best method to investigate the thermodynamic stability of those compounds [8,9]. Since then, RSC has been used in Lisbon to study the thermochemistry of many organometallic compounds, aiming to examine the systematics of metal-ligand bond dissociation enthalpies and to explore new methods to predict the enthalpies of reactions involving transition metal compounds. Some of this work, now shared by people from three institutions (Instituto Superior Técnico, Faculdade de Ciências da Universidade de Lisboa, and Instituto Tecnológico e Nuclear), has been reviewed elsewhere [10,11].

Information about the stability of molecules and bonds has been steadily accumulating throughout the past two decades. The development of new experimental methodologies, in solution and in the gas phase, allowed the thermochemical study of neutral and ionic molecular species that are not amenable to classical calorimetry. A pictorial overview of the main methods - old and new - is shown in Figure 2. Here, it is deliberately stressed that bond energies (or bond enthalpies), rather than enthalpies of formation, are the goal of most studies in modern thermochemistry. As noted above, there are many molecules for which only bond dissociation enthalpy data are available, this being especially true for organometallic compounds [11,12]. But perhaps the most striking feature of Figure 2 is the large number of techniques that have contributed to the present knowledge in Molecular Thermochemistry. Actually, the number is even higher than indicated, because some gas phase techniques and some auxiliary methodologies have been omitted. Why then, such a variety? The answer is quite simple: the investigation of the stability of any molecule is a very specific task. The choice of a given technique is often dictated by the nature of atoms that constitute the molecule, by its physical state, and by its lifetime.

Despite all the efforts to increase the amount and the quality of thermochemical data, there are still many important gaps to be filled. Today, the databases of enthalpies of formation and bond dissociation enthalpies are fairly large [12-17], particularly for organic and inorganic substances, but there is (and there will always be) a large difference between the sizes of those databases and the virtually infinite number of known molecules. As a result, several empirical methods for estimating those data have been developed [4,13,17-20]. It can be

anticipated that these research lines will have increased importance in the future, but their progress depends on the availability of experimental data, needed to test the reliability of the estimates and also to "calibrate" quantum chemical calculations. Computational Chemistry methods have been playing a rather significant role in Molecular Thermochemistry and some of them afford highly reliable results, for many species. The fast improvement of hardware and software will strengthen that role and Computational Chemistry will replace many experimental methodologies.

From what has been said in this short outline, which included a short digression through the origins of the "Lisbon group", it seems clear that Molecular Thermochemistry is not a science from the past. No doubt that some of the techniques in Figure 2 are over 100 years old. It is also true that the available empirical estimation schemes and Computational Chemistry methods are often reliable enough to replace laboratory work. But it is also a fact that many more enthalpies of formation and bond enthalpy data are needed to improve our understanding of chemical structure and reactivity, whose relationship is in the core of modern chemical research [21].

The present interest in Molecular Thermochemistry is best demonstrated by the variety of recent experimental techniques, depicted in Figure 2, which have extended our ability to study the energetics of species like short-lived ions and radicals. Furthermore, the selected examples addressed in the following paragraphs show that the use of "classical" methods, such as calorimetry, still have a significant and unreplaceable role. The most classical of them all, combustion calorimetry, is fundamental to probe the thermochemistry of molecules such as buckminsterfullerene. Finally, a single example of an

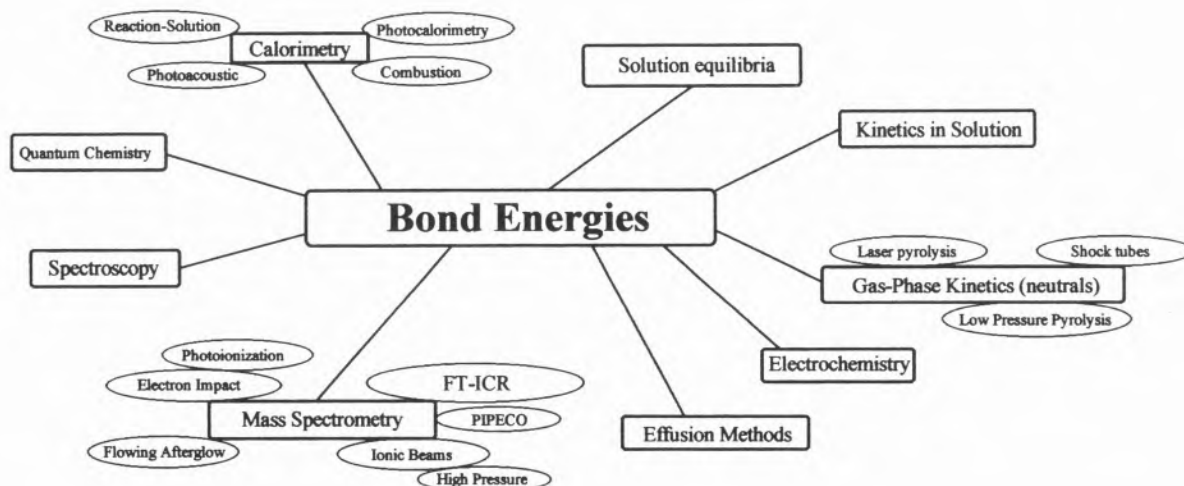
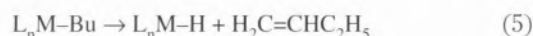
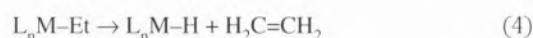


Figure 2 – Methods used to study the thermochemistry of chemical bonds.

area where the present thermochemical knowledge is rather scanty: the solvation of free radicals. The combination of gas-phase and solution data, obtained from some of the techniques displayed in Figure 2, will refine our understanding of the solvent effect on the chemical behavior of those species.

## 2. $\beta$ -Hydride Elimination

As stated above, bond dissociation enthalpy data,  $DH^\circ(M-L)$  ( $M$  = metal center;  $L$  = ligand), obtained from reaction-solution calorimetry experiments, have been used, by us and others, to investigate trends in the chemical reactivity of organometallic complexes. The scope of these studies can be illustrated by the discussion of the  $\beta$ -hydride elimination reaction (Scheme 1), which is the most important decomposition pathway for transition metal, lanthanide and actinide alkyl complexes containing  $\beta$ -hydrogen substituents, and a key elementary step in many catalytic cycles [22]. For ethyl (Et) and butyl (Bu) derivatives the reaction can be represented by equations 4 and 5, respectively.



$L_nM$  is a coordinatively unsaturated metal complex with  $n$  ancillary ligands,  $L$ . The enthalpies of reactions 4 and 5,  $\Delta_r H_m^\circ$  (4) and  $\Delta_r H_m^\circ$  (5), can be related to bond dissociation enthalpies by equations 6 and 7, respectively.

$$\Delta_r H_m^\circ(4) = DH^\circ(M-Et) + DH^\circ(C_2H_4-H) - DH^\circ(M-H) \quad (6)$$

$$\Delta_r H_m^\circ(5) = DH^\circ(M-Bu) + DH^\circ(C_4H_8-H) - DH^\circ(M-H) \quad (7)$$

Table 1 lists enthalpies of  $\beta$ -hydride elimination for various organometallic systems. These values were calculated from  $DH^\circ(C_2H_4-H) = 151.5 \pm 4.0$  kJ/mol [11,13] and  $DH^\circ(C_4H_8-H) = 144.1 \pm 8.0$  kJ/mol [11,13], and from the experimentally measured or estimated  $M-H$ ,  $M-Et$  and  $M-Bu$  bond dissociation enthalpy data indicated in the Appendix [10,11,23-36]. Analysis of Table 1 suggests that, with the notable exception of the rhodium system, the reaction is more endothermic, and therefore less favorable, for actinides and early transition metal complexes, than for late transition metal complexes. In addition,  $\beta$ -hydride elimination from a butyl ligand to give 1-butene is more favorable than the corresponding reaction for an ethyl ligand.

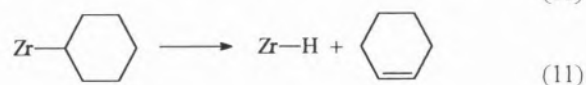
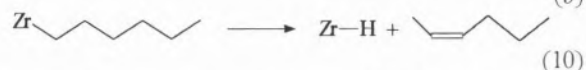
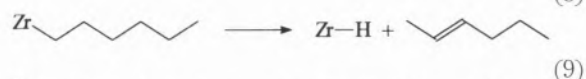
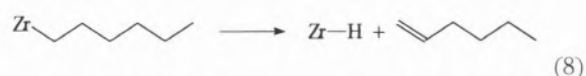
In reactions 4 and 5 a terminal alkene is generated by  $\beta$ -hydride elimination. It is interesting to compare the thermochemistry of this type of reaction with that of a reaction in which a non-terminal alkene is formed, and also with the thermochemistry of a reaction that yields a

**Table 1.** Enthalpies of  $\beta$ -hydride elimination reaction for various transition metal and actinide systems (reactions 4 and 5; see text and Appendix). Data in kJ/mol.

Complex <sup>a</sup>	$\Delta_r H_m^\circ$	
	L = Et	L = Bu
Th(Cp <sup>+</sup> ) <sub>2</sub> L <sub>2</sub>	82±11	63±14
Th(Cp <sup>+</sup> ) <sub>2</sub> (O- <i>t</i> -Bu)L	94±11	72±18
Th(Cp <sup>+</sup> ) <sub>2</sub> (Cl)L	77±11	66±16
Th(Cp <sup>+</sup> ) <sub>2</sub> [OCH( <i>t</i> -Bu) <sub>2</sub> ]L	113±18	102±18
U(Cp <sup>+</sup> ) <sub>2</sub> [OSi( <i>t</i> -Bu)(Me) <sub>2</sub> ]L	109±10	98±14
Zr(Cp <sup>+</sup> ) <sub>2</sub> L <sub>2</sub>	79±7	68±12
Hf(Cp <sup>+</sup> ) <sub>2</sub> L <sub>2</sub>	94±11	72±15
Mo(Cp) <sub>2</sub> L <sub>2</sub>	51±13	41±17
Mo(Cp)(CO) <sub>3</sub> L	55±13	44±15
W(Cp) <sub>2</sub> L <sub>2</sub>	44±8	33±13
Mn(CO) <sub>5</sub> L	76±12	65±16
Rh(tmp)L	104	93
Ir(Cl)(CO)(PMe <sub>3</sub> ) <sub>2</sub> (t)L	39±9	20±22
Pt(PR <sub>3</sub> ) <sub>2</sub> (Cl)L	51±37	40±38

<sup>a</sup> Cp<sup>+</sup> =  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>; tmp = 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrinato dianion.

cyclic alkene from a cyclic alkyl. Recent reaction-solution calorimetry studies of Zr(Cp)<sub>2</sub>(Cl)R ( $R$  = H, alkyl) complexes allow us to make these comparisons (reactions 8-11) [37].



The enthalpies of reactions 8-11 are given by equations 12-15 where Hx = hexyl, Cy = cyclohexyl,

$$\Delta_r H_m^\circ(8) = DH(Zr-Hx) + DH(1\text{-hexene-H}) - DH(Zr-H) \quad (12)$$

$$\Delta_r H_m^\circ(9) = DH(Zr-Hx) + DH(E\text{-}2\text{-hexene-H}) - DH(Zr-H) \quad (13)$$

$$\Delta_r H_m^\circ(10) = DH(Zr-Hx) + DH(Z\text{-}2\text{-hexene-H}) - DH(Zr-H) \quad (14)$$

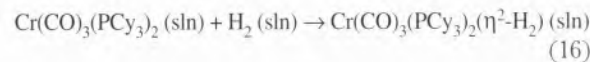
$$\Delta_r H_m^\circ(11) = DH(Zr-Cy) + DH(CY\text{-hexene-H}) - DH(Zr-H) \quad (15)$$



By using,  $DH^\circ(\text{Zr-H}) = 364 \pm 5$  kJ/mol [37],  $DH^\circ(\text{Zr-Hx}) = 317 \pm 10$  kJ/mol [37],  $DH^\circ(\text{Zr-Cy}) = 319 \pm 7$  kJ/mol [37],  $DH^\circ(1\text{-hexene-H}) = 141.4 \pm 8.2$  kJ/mol [11,13],  $DH^\circ(E\text{-}2\text{-hexene-H}) = 131.0 \pm 8.1$  kJ/mol [11,13],  $DH^\circ(Z\text{-}2\text{-hexene-H}) = 132.6 \pm 8.1$  kJ/mol [11,13],  $DH^\circ(\text{cyclohexene-H}) = 155.1 \pm 4.0$  kJ/mol [11,13], it is concluded that  $\Delta_r H_m^\circ(8) = 94 \pm 14$  kJ/mol,  $\Delta_r H_m^\circ(9) = 84 \pm 14$  kJ/mol,  $\Delta_r H_m^\circ(10) = 86 \pm 14$  kJ/mol, and  $\Delta_r H_m^\circ(11) = 110 \pm 10$  kJ/mol. These results indicate that, at least for this Zr system, it is less favorable to obtain a terminal alkene from a linear alkyl ligand coordinated to a metal center by  $\beta$ -hydride elimination, than a non-terminal alkene. It can also be concluded that it is less favorable to generate a cyclic alkene from the parent coordinated cyclic alkyl, than a linear (terminal or non-terminal) alkene from the parent alkyl ligand. Note that, since  $DH^\circ(\text{Zr-Hx}) \approx DH^\circ(\text{Zr-Cy})$ , this last conclusion is mainly due to the fact that  $DH^\circ(\text{cyclohexene-H})$  considerably exceeds  $DH^\circ(1\text{-hexene-H})$ ,  $DH^\circ(E\text{-}2\text{-hexene-H})$ , and  $DH^\circ(Z\text{-}2\text{-hexene-H})$ .

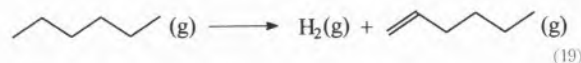
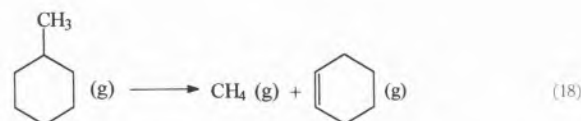
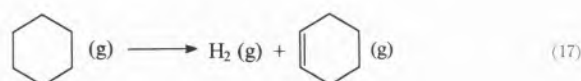
We have been discussing reactivity trends based on the exothermicity or endothermicity of a reaction, more exothermic meaning more favorable conversion of reactants into products. However, as stated above, the thermodynamic driving force of a chemical reaction is measured by the Gibbs energy of reaction, which, in addition to an enthalpic contribution also includes an entropic term (equation 1). A large and negative  $\Delta_r H_m^\circ$  (a very exothermic reaction) in conjunction with a large and positive  $T\Delta_r S_m^\circ$  will favor the yield of the reaction.

It has already been noted that the enthalpic term usually dominates the entropic term around room temperature. This explains why  $\Delta_r S_m^\circ$  is frequently ignored in the discussion of reaction thermochemistry. In some cases, however,  $T\Delta_r S_m^\circ$  makes an important contribution or even determines the sign of  $\Delta_r G_m^\circ$ . For example, studies of reaction 16 in tetrahydrofuran, lead to  $\Delta_r H_m^\circ(16) = -30.5$  kJ/mol and  $T\Delta_r S_m^\circ(16) = -31.9$  kJ/mol, at 298.15 K [38]. This corresponds to  $\Delta_r G_m^\circ = 1.4$  kJ/mol. In this case, ignoring the entropic contribution (i.e. making  $\Delta_r G_m^\circ \approx \Delta_r H_m^\circ$ ) results in an extremely large error in the value of the equilibrium constant ( $K = 1.8 \times 10^5$  instead of  $K = 0.57$ ).



Fortunately, the entropy of a reaction essentially depends on the net change of the internal and external degrees of freedom between reactants and products and not on the types of bonds broken and formed. Therefore,  $\Delta_r S_m^\circ$  for organometallic reactions can frequently be identified with known  $\Delta_r S_m^\circ$  values for model organic or inorganic reactions that mimic the changes in degrees of freedom of the organometallic reaction [39]. For example, an estimate of the entropy of reaction 11 can be made by using reactions 17 or 18 as models. The values of  $T\Delta_r S_m^\circ$  at 298.15 K, for reactions

17 and 18, are 42.7 kJ/mol and 45.8 kJ/mol, respectively [16,40]. Note that, although different reactants and products are involved in reactions 17 and 18, the corresponding entropy changes are similar. It is therefore expected that the  $T\Delta_r S_m^\circ$  value for reaction 11 can be identified with the average of the two above values, ca. 44 kJ/mol, with a small error (less than 5 kJ/mol). The exercise can be repeated for reaction 8 by using reactions 19 and 20 as models. In these cases,  $T\Delta_r S_m^\circ = 37.9$  kJ/mol and  $T\Delta_r S_m^\circ = 42.6$  kJ/mol, respectively. The values are very similar to those obtained for reactions 17 and 18, showing that, in general, for  $\beta$ -hydride eliminations an entropic contribution of ca. 35-45 kJ/mol should be considered. This reaction is thus favored by a  $T\Delta_r S_m^\circ$  term which may offset  $\Delta_r H_m^\circ$  for late transition metal systems (Table 1).



### 3. Alkaline Metal Alkoxides

The thermochemistry of sodium and lithium alkoxides has been the subject of two publications from our group [41,42]. This work, which has now been extended to other metals (K, Rb, Cs, Mg, Ca) [43], is recalled here to illustrate a typical application of reaction-solution calorimetry results in the area of solid-state Inorganic Chemistry. The data will also be used to make a very brief description of a procedure for estimating standard enthalpies of formation of inorganic and organometallic compounds, which we like to call Tina's method, after our colleague (Clementina Teixeira, IST) who first suggested it.

The standard enthalpies of formation of the crystalline compounds MOR, where M = Li or Na, and R is an alkyl group, have been derived from the enthalpies of their reactions with water or with aqueous hydrochloric acid solutions. As shown in Figure 3, when  $\Delta_r H_m^\circ(\text{MOR}, \text{cr})$  are plotted against the standard enthalpies of forma-

tion of the respective liquid alcohols,  $\Delta_f H_m^\circ(\text{ROH}, 1)$ , good linear correlations are observed in the case of  $R = n\text{-alkyl}$ . The relationships are described by equation 21, which can then be used to estimate enthalpies of formation of other  $n\text{-alkoxides}$  by using literature data for  $\Delta_f H_m^\circ(\text{ROH}, 1)$ .

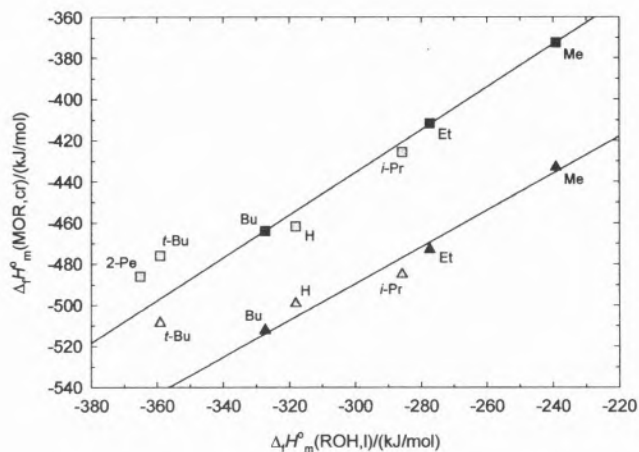


Figure 3 – Standard enthalpies of formation of sodium (squares) and lithium (triangles) alkoxides versus the standard enthalpies of formation of the corresponding alcohols.

$$\Delta_f H_m^\circ(\text{MOR}, \text{cr}) = a \Delta_f H_m^\circ(\text{ROH}, 1) + b \quad (21)$$

The method illustrated by this equation has been applied to numerous organic, inorganic and organometallic families of molecules and subject to a detailed analysis [18,37,41,42,44-54]. Here only a few aspects will be emphasized. First, note that the points for  $R = t\text{-Bu}$  lie clearly above the line, i.e. their enthalpies of formation are higher than expected from the enthalpy of formation of  $t\text{-butyl}$  alcohol. It has been suggested that these destabilizations may be related to different solid state structures of the alkoxides rather than to steric effects [42]. However, it has also been shown that a simple modification of equation 21, which includes the group electronegativities of RO in the molecules MOR ( $M = \text{Li}, \text{Na}$ ) and ROH, allows to fit all the experimental data within a few kilojoules, indicating that the “high” values have - at least in part - an electronic origin [42].

Another interesting use of equation 21 is that it enables to estimate gas-phase MO-R bond dissociation enthalpies. For the alkoxides that fit the correlation, it is possible to conclude that the differences  $DH^\circ(\text{M-OR}) - DH^\circ(\text{RO-H})$  are approximately constant [41,42]. As the O-H bond dissociation enthalpies in alcohols fall in a narrow range, with an average of ca. 499 kJ/mol,  $\langle DH^\circ(\text{Li-OR}) \rangle = 394$  kJ/mol and  $\langle DH^\circ(\text{Na-OR}) \rangle = 280$  kJ/mol could be derived [41,42].

The strongly ionic nature of the MOR bond has been confirmed by calculating the lattice energies,  $U^\circ$ ,

of the alkoxides, through the Born-Haber cycle shown in Figure 4, or, alternatively, by deriving the heterolytic MOR bond dissociation enthalpies,  $DH^\circ(\text{M}^+ - \text{OR}^-)$ , through the cycle in Figure 5. It was found that the lattice energies of the alkoxides are only less than ca. 10% lower than the lattice energies of the hydroxides,  $U^\circ(\text{NaOH}) = 886.4$  kJ/mol and  $U^\circ(\text{LiOH}) = 1028.4$  kJ/mol, which have a rather ionic M-OR bond. A similar variation has been observed for the heterolytic bond dissociation enthalpies.

The thermochemical cycle in Figure 5 also affords estimates of the sublimation enthalpies of the alkoxides, by using the  $DH^\circ(\text{M-OR})$  and  $U^\circ(\text{MOR})$  data. This is particularly useful because these quantities are not easy to obtain experimentally for many ionic-type compounds. It has been concluded that  $\Delta_{\text{cr}}^\circ H_m^\circ(\text{MOR})$  for the  $n\text{-alkoxides}$  are in the range of 215-230 kJ/mol [41, 42]. Incidentally, the value calculated for LiOMe, 216 kJ/mol, together with the experimental value for  $\Delta_f H_m^\circ(\text{LiOMe}, \text{cr}) = -433.0 \pm 2.4$  kJ/mol, leads to  $\Delta_f H_m^\circ(\text{LiOMe}, \text{g}) = -217$  kJ/mol, which is in excellent agreement with a theoretical result derived by Sana *et al.*, -214 kJ/mol [55].

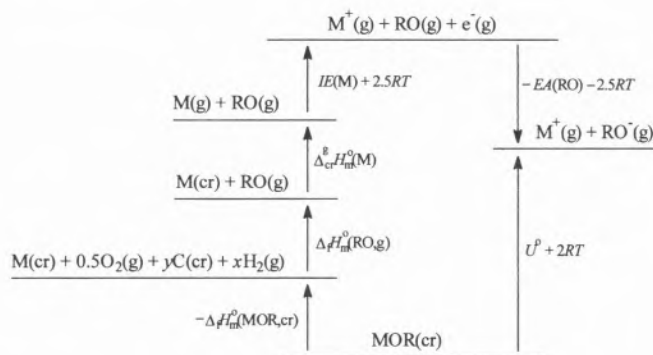


Figure 4 – Born-Haber cycle for alkaline metal alkoxides.  $IE(M)$  and  $EA(RO)$  are the ionization energy of the alkaline metal and the adiabatic electron affinity of the alkoxy radical, respectively.

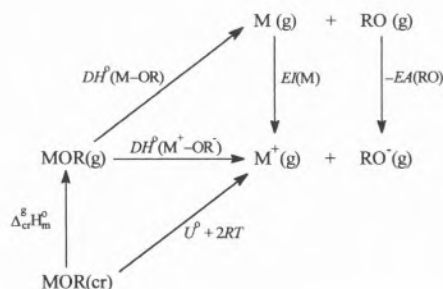


Figure 5 – Thermochemical cycle for estimating the enthalpies of sublimation of alkaline metal alkoxides.

#### 4. They came from outer space!

The search for complex molecules in the shell of gas and dust surrounding red giant stars, and for the origin of the diffuse interstellar bands, led to what is probably the most revolutionary discovery in chemistry in the latest years - the fullerenes [56]. Until 1985, only six crystalline forms of carbon were known: two forms of graphite, two forms of diamond, chaoit and carbon(VI). But in September 1985, a new form of carbon,  $C_{60}$ , shaped like a soccer ball (Figure 6), was

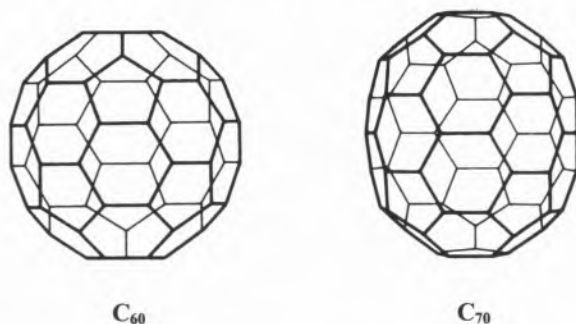


Figure 6 - The structures of the two most famous fullerenes:  $C_{60}$  and  $C_{70}$ .

postulated by a group led by Kroto from Sussex University, U. K., and Smalley and Curl, from Rice University, U. S. A. [57]. The existence of this species was proposed from mass spectral evidence obtained in experiments involving laser vaporization of graphite in a laser-supersonic cluster beam apparatus. The  $C_{60}$  molecule and the related  $C_{70}$  (Figure 6) were finally isolated in 1990 by a team composed of Krätschmer and Fostiropoulos from the Max Planck Institute of Nuclear Physics in Heidelberg, Germany, and Lamb and Huffman, from the University of Arizona, U. S. A. [58]. There is now a whole galaxy of fullerenes, extending well beyond  $C_{100}$ , as well as other carbon structures such as carbon nanotubes. The chemistry of the fullerenes is also undergoing rapid development and many organic, inorganic, and organometallic derivatives have been prepared [59]. For the discovery of the fullerenes Kroto, Curl and Smalley were awarded the 1996 Nobel Prize in Chemistry.

The enthalpies of formation of  $C_{60}$  and  $C_{70}$  are key values to establish the thermodynamic stability of these molecules, and also to assess the results of Computational Chemistry methods that are used to predict the properties of the fullerenes and their mechanisms of formation. Microcombustion calorimetric experiments in our laboratory led to  $\Delta_f H_m^\circ(C_{60}, cr) = 2278.1 \pm 14.4$  kJ/mol and  $\Delta_f H_m^\circ(C_{70}, cr) = 2577.8 \pm 16.2$  kJ/mol, at 298.15 K [60,61]. Statistical mechanical calculations of

the heat capacities of gaseous  $C_{60}$  and  $C_{70}$  as a function of the temperature, in conjunction with a critical survey of the literature data for their heat capacities in the crystalline state and their enthalpies of sublimation, enabled to derive the enthalpies of formation of gaseous  $C_{60}$  and  $C_{70}$ , at 298.15 K [60-62]. The obtained results are compared in Table 2 with other experimental [60,61,63-68] and theoretically predicted [69-88] values, reported in the literature.

The agreement between the experimental results in Table 2 is far from satisfactory. It is however sufficient to set reliable upper and lower limits for  $\Delta_f H_m^\circ(C_{60}, g)$  and  $\Delta_f H_m^\circ(C_{70}, g)$ . These limits can be used to assess the theoretical predictions, which show much larger discrepancies (Table 2). In general, the results of the *ab initio* methods, or of semi-empirical calculations specifically parameterized for fullerenes, are closer to the experimental values. It is also interesting to note that the empirical group additivity method of Armitage and Bird [78], which is based on enthalpy of formation data for polycyclic aromatic hydrocarbons, predicts the enthalpies of formation of  $C_{60}$  and  $C_{70}$  with remarkable accuracy.

The data in Table 2 also indicate that the enthalpy of formation per carbon atom,  $\Delta_f H_m^\circ/n$  ( $n$  = number of carbon atoms in the fullerene), is smaller for  $C_{70}$  than for  $C_{60}$ . This conclusion supports the theoretical prediction that a general tendency exists for a decrease of  $\Delta_f H_m^\circ/n$ , towards zero, with the increasing size of the fullerenes [89] - the bigger the fullerene the closer its structure becomes to that of graphite, which has  $\Delta_f H_m^\circ/n = 0$ . It also indicates that, at room temperature,  $C_{70}$  is thermodynamically more stable than  $C_{60}$ .

The carbon-carbon mean bond dissociation enthalpies,  $\overline{DH}^\circ(C_i - C_j)$ , for  $C_{60}$  and  $C_{70}$ , can be derived from equation 22. Here,  $m$  is the number of bonds in the fullerene ( $m = 90$  for  $C_{60}$  and  $m = 105$  for  $C_{70}$ ) and  $\Delta_f H_m^\circ$  is the enthalpy of atomization of the fullerene, i. e. the enthalpy of reaction 23.

$$\overline{DH}^\circ(C_i - C_j) = \frac{\Delta_f H_m^\circ}{m} \quad (22)$$



The enthalpies of atomization of  $C_{60}$  and  $C_{70}$  can be calculated from  $\Delta_f H_m^\circ(C, g) = 716.68 \pm 0.45$  kJ/mol [90] and the enthalpies of formation of the fullerenes in Table 2. When these data are used with equation 22 it is possible to conclude that  $\overline{DH}^\circ(C_i - C_j)$  is in the range 448.9–450.5 kJ/mol for  $C_{60}$  and in the range 451.2–453.2 kJ/mol for  $C_{70}$ . Thus,  $\overline{DH}^\circ(C_i - C_j)$  is slightly larger in  $C_{70}$  than in  $C_{60}$ , as expected from the above conclusion that, at room temperature,  $C_{70}$  is thermodynamically more stable than  $C_{60}$ . For comparison, the bond enthalpy terms for single, double, and aromatic C–C bonds are  $E(C-C) = 357.6$  kJ/mol,  $E(C=C) = 556.5$  kJ/mol, and  $E(C_b-C_b) = 498.6$  kJ/mol [17].

**Table 2.** Comparison between experimental and theoretical results for the enthalpies of formation of C<sub>60</sub> and C<sub>70</sub> in the gas phase.

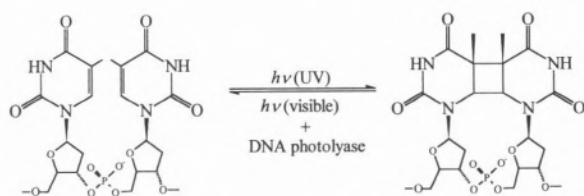
$\Delta_f H_m^\circ(\text{g}) / (\text{kJ/mol})$		Method	Reference
C <sub>60</sub>	C <sub>70</sub>		
1197	1443	MMP2	69
2175	2438	MM2	70
2217		<i>ab initio</i> SCF	71
	2611	MNDO calibrated using experimental data for C <sub>60</sub>	72
2322	2465	Tight-binding hamiltonian	73
2398	2676	MM3	74
2401	2665	MM3	64, 75
2435		<i>ab initio</i> STO-3G and extrapolation method	76
2510	2661	<i>ab initio</i> HF-LYP/DZP//MNDO	77
2653	2714	Group additivity method	78
	2785	MNDO calibrated using experimental data for C <sub>60</sub>	79
2615	2790	<i>ab initio</i> HF/STO-3G	74
2812		<i>ab initio</i> HF/6-31G*/STO-3G and group additivity method	80
2884	3051	MNDO calibrated using data for graphite	69, 81
3012		<i>ab initio</i> STO-3G and group additivity method	82
3392	3699	PM3	72, 79, 83
	3700	PM3	84
3633	3930	MNDO, standard parameters	72, 79
3637	3954	MNDO, standard parameters	81, 83, 85-87,
4069	4443	AM1	72, 79
4072	4485	AM1	69
4092		PRDDO	88
2459±14 <sup>a</sup>	2788±21 <sup>b</sup>	Experimental	60,61
2454±15 <sup>a</sup>	2585±22 <sup>b</sup>	Experimental	63
2508±17 <sup>a</sup>	2765±22 <sup>b</sup>	Experimental	64
2463±10 <sup>a</sup>		Experimental	65
2603±14 <sup>a</sup>		Experimental	66
2536±15 <sup>a</sup>		Experimental	67
2540±10 <sup>a</sup>		Experimental	68

<sup>a</sup> Calculated using  $\Delta_{\text{cr}} H_m^\circ(\text{C}_{60}) = 181 \pm 2 \text{ kJ/mol}$ , at 298.15 K [62].

<sup>b</sup> Calculated using  $\Delta_{\text{cr}} H_m^\circ(\text{C}_{70}) = 210 \pm 13 \text{ kJ/mol}$ , at 298.15 K, selected in reference 61.

## 5. Energetics of DNA Repair by DNA Photolyases

Exposure of DNA to ultraviolet radiation results in the formation of pyrimidine dimers, as a consequence of a cycloaddition reaction between two neighbor pyrimidines in the double helix (Scheme 2) [91]. This reac-



Scheme 2

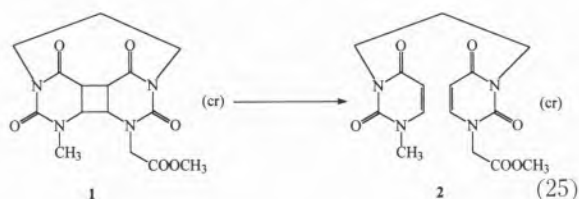
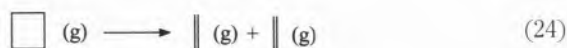
tion constitutes the highest quantum yield damage caused to DNA by UV-light [91]. In a wide variety of living organisms, the lesion can be reversed, in a light-assisted process, by enzymes called DNA photolyases (Scheme 2) [92].

As can be seen in Scheme 2, the repair process involves the cleavage of a cyclobutane ring. For reaction 24, at 298.15 K,  $\Delta_f H_m^\circ = 76.5 \pm 0.8 \text{ kJ/mol}$  [13] and  $T\Delta_r S_m^\circ = 51.4 \text{ kJ/mol}$  [40], implying that  $\Delta_r G_m^\circ = 25.1 \text{ kJ/mol}$ . This result could suggest that the repair process might be endergonic. In order to test this hypothesis and to understand the driving force of the enzyme action, the enthalpies of formation of compounds **1** and **2** (equation 25) were determined by microcombustion calorimetry. The obtained values,  $\Delta_f H_m^\circ(\mathbf{1}, \text{cr}) = -1006.6 \pm 3.7 \text{ kJ/mol}$  and  $\Delta_f H_m^\circ(\mathbf{2}, \text{cr}) = -1116.6 \pm 3.7 \text{ kJ/mol}$ , lead to an enthalpy of  $-110.0 \pm 5.2 \text{ kJ/mol}$  for the clea-



vage of the model photodimer **1** (reaction 25) [93]. This reaction should also have a positive entropy contribution, and therefore, contrary to reaction 24, is exergonic. In conclusion, although photoenzymes can induce strongly endergonic reactions through the formation of a high energy enzyme substrate complex, this is not the case of DNA photolyases, as suggested by our study: according to the model used, the role of the enzyme is purely kinetic.

It is also interesting to note that the exothermicity of reaction 25, when compared to the endothermicity of reaction 24, reflects the additional strain in the pyrimidine photodimer, when compared to the simple cyclobutane ring, and the formation of the more stable delocalized double bond in the pyrimidine ring.



## 6. Conclusion

The four examples described in the previous paragraphs, which stemmed from our own research interests or were the result of fruitful collaborations with other groups, illustrate how we have been using thermochemical methodologies to examine several issues in different areas of Chemistry. As hinted by the discussions above, some of these problems are still being addressed by more laboratory work. The thermodynamic stability of organometallic substances and metal-ligand bonds, for instance, which has been at the center of our research interests for many years, still plays a significant role in our group's activity. Besides new experiments and the development of estimation methods, the work in this area now includes a general critical analysis of all the data available in the literature [12].

The above case-studies involved only the two main techniques that so far have been used in our research – reaction-solution calorimetry and microcombustion calorimetry. More recently, other experimental methods (photocalorimetry, photoacoustic calorimetry, and ion-cyclotron resonance mass spectrometry) have been added to our thermochemical tools, allowing to extend the range of problems we wish to address. Photocalorimetry has enabled to probe the thermochemistry of some light-induced reactions [94]. Photoacoustic calorimetry, and ion-cyclotron resonance mass spectrometry will enable, for example, to investigate the solvation energetics of transient species.

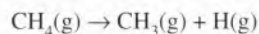
## Acknowledgements

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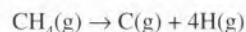
## Appendix

The definition of the most common thermochemical quantities, such as *standard enthalpy of formation*, can be found in Physical Chemistry textbooks [1]. Other, more specific, thermochemical quantities, referred to in this paper, are discussed, for example, by Cox and Pilcher [17]. Nevertheless, for the sake of clarity, some definitions are given below.

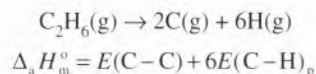
Consider the methane molecule. The C–H *bond dissociation enthalpy*,  $DH^\circ(\text{CH}_3 - \text{H})$ , is the enthalpy of the following reaction:



The *mean C–H bond dissociation enthalpy*,  $DH^\circ(\text{C–H})$ , is one fourth of the *enthalpy of atomization* of methane:



The concept of *bond enthalpy term*,  $E$ , can be better illustrated by using ethane as an example. The C–C and C–H bond enthalpy terms in this molecule are the quantities whose sum reproduces the enthalpy of atomization of  $\text{C}_2\text{H}_6$ . In this atomization reaction, one C–C bond and six primary C–H bonds are cleaved:



All species above are in their standard states and at 298.15 K.

Bond dissociation enthalpies (and bond enthalpy terms) should only be defined in the ideal gas phase because otherwise they would be affected by intermolecular interactions. However, from a practical point of view, *solution-phase bond dissociation enthalpies*,  $DH_{\text{sln}}^\circ$ , are often used, since many important reactions occur in solution. Also, reliable solvation enthalpy data are very scarce, hindering the calculation of gas phase values from solution experiments. The C–H bond dissociation enthalpy of methane in solution,  $DH_{\text{sln}}^\circ(\text{CH}_3 - \text{H})$ , would be defined as above, with all the species (reactant and products) in solution, at infinite dilution.

Complex	$DH^\circ(M-L)$ or $\overline{DH^\circ}(M-L)$		
	L = H	L = Et	L = Bu
Th(Cp*) <sub>2</sub> L <sub>2</sub>	(388±6) <sup>b</sup>	318±8	307±9
Th(Cp*) <sub>2</sub> (O- <i>t</i> -Bu)L	(388±6) <sup>b</sup>	330±8	316±15
Th(Cp*) <sub>2</sub> (Cl)L	(388±6) <sup>b</sup>	313±8	(310±12) <sup>c</sup>
Th(Cp*) <sub>2</sub> [OCH( <i>t</i> -Bu) <sub>2</sub> ]L	389±6	(3501±7) <sup>d</sup>	347±15
U(Cp*) <sub>2</sub> [OSi( <i>t</i> -Bu)(Me) <sub>2</sub> ]L	342±5	(299±7) <sup>e</sup>	(296±10) <sup>e</sup>
Zr(Cp*) <sub>2</sub> L <sub>2</sub>	339±2	(266±5) <sup>f</sup>	(263±8) <sup>f</sup>
Hf(Cp*) <sub>2</sub> L <sub>2</sub>	346±7	(288±8) <sup>g</sup>	274±10
Mo(Cp) <sub>2</sub> L <sub>2</sub>	257±8	156±9	154±12
Mo(Cp)(CO) <sub>3</sub> L	282±6	(185±11) <sup>h</sup>	(182±11) <sup>h</sup>
W(Cp) <sub>2</sub> L <sub>2</sub>	311±4	(203±5) <sup>i</sup>	(200±9) <sup>i</sup>
Mn(CO) <sub>5</sub> L	245±10	(169±6) <sup>j</sup>	(166±9) <sup>j</sup>
Rh(tmp)L	251	203	(200) <sup>k</sup>
Ir(Cl)(CO)(PMe <sub>3</sub> ) <sub>2</sub> (I)L	C + (109±15) <sup>l</sup>	C – (41±0)	[C – (15±14)] <sup>m</sup>
<i>trans</i> -Pt(PR <sub>3</sub> ) <sub>2</sub> (Cl)H	307±37 (R = Ph)	206 (R = Et)	(203) <sup>n</sup>

<sup>a</sup> Values in parentheses are estimates.

<sup>b</sup> Average of  $DH^\circ(\text{Th-H}) = 384 \pm 6$  kJ/mol in Th(Cp\*)<sub>2</sub>[O-2,6-(*t*-Bu)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]H,  $DH^\circ(\text{Th-H}) = 389 \pm 6$  kJ/mol in Th(Cp\*)<sub>2</sub>[O-CH(*t*-Bu)<sub>2</sub>]H, and  $\overline{DH^\circ}(\text{Th-H}) = 390$  kJ/mol in [Th(Cp\*)<sub>2</sub>H]<sub>2</sub>.

<sup>c</sup> Estimated from  $DH^\circ(\text{Th-Et}) = 313 \pm 8$  kJ/mol,  $DH^\circ(\text{Et-H}) = 421 \pm 4$  kJ/mol, and  $DH^\circ(\text{Bu-H}) = 418 \pm 8$  kJ/mol, by assuming that  $DH^\circ(\text{Th-Et}) - DH^\circ(\text{Th-Bu}) = DH^\circ(\text{Et-H}) - DH^\circ(\text{Bu-H})$ .

<sup>d</sup> Estimated from  $\overline{DH^\circ}(\text{Th-Bu}) = 347 \pm 15$  kJ/mol, by using the assumption in note c.

<sup>e</sup> Estimated from  $DH^\circ(\text{U-Me}) = 317 \pm 6$  kJ/mol, in U(Cp\*)<sub>2</sub>[OSi(*t*-Bu)(Me)<sub>2</sub>]Me,  $DH^\circ(\text{Me-H}) = 439.4 \pm 0.8$  kJ/mol,  $DH^\circ(\text{Et-H}) = 421 \pm 4$  kJ/mol, and  $DH^\circ(\text{Bu-H}) = 418 \pm 8$  kJ/mol, by assuming that  $DH^\circ(\text{U-Me}) - DH^\circ(\text{U-Et}) = DH^\circ(\text{Me-H}) - DH^\circ(\text{Et-H})$  and  $DH^\circ(\text{U-Me}) - DH^\circ(\text{U-Bu}) = DH^\circ(\text{Me-H}) - DH^\circ(\text{Bu-H})$ .

<sup>f</sup> Estimated from  $\overline{DH^\circ}(\text{Zr-Me}) = 284 \pm 2$  kJ/mol, in Zr(Cp\*)<sub>2</sub>Me<sub>2</sub>, by using the method described in note e.

<sup>g</sup> Estimated from  $\overline{DH^\circ}(\text{Hf-Me}) = 306 \pm 7$  kJ/mol, in Hf(Cp\*)<sub>2</sub>Me<sub>2</sub>, by using the method described in note e.

<sup>h</sup> Estimated from  $\overline{DH^\circ}(\text{Mo-Me}) = 203 \pm 8$  kJ/mol, in Mo(Cp)(CO)<sub>3</sub>Me, by using the method described in note e.

<sup>i</sup> Estimated from  $\overline{DH^\circ}(\text{W-Me}) = 221 \pm 3$  kJ/mol, in W(Cp)<sub>2</sub>Me<sub>2</sub>, by using the method described in note e.

<sup>j</sup> Estimated from  $\overline{DH^\circ}(\text{Mn-Me}) = 187 \pm 4$  kJ/mol, in Mn(CO)<sub>5</sub>Me, by using the method described in note e.

<sup>k</sup> Estimated from  $\overline{DH^\circ}(\text{Rh-Et}) = 203$  kJ/mol, in Rh(tmp)Et, by using the assumption in note c.

<sup>l</sup> C is an arbitrary constant.

<sup>m</sup> Estimated from  $DH^\circ(\text{Ir-Me}) = C + (6 \pm 11)$  kJ/mol in Ir(Cl)(CO)(PMe<sub>3</sub>)<sub>2</sub>(I)Me, using the assumption indicated in note e.

<sup>n</sup> Estimated from  $DH^\circ(\text{Pt-Et}) = 206$  kJ/mol in *trans*-Pt(PMe<sub>3</sub>)<sub>2</sub>(Cl)Et, using the method indicated in note c.

## References

1. P. W. Atkins, *Physical Chemistry* (5th ed.); Oxford University Press: Oxford, 1994.
2. G. W. Burton, K. U. Ingold, *Acc. Chem. Res.* **19** (1986) 194.
3. G. W. Burton, T. Doba, E. J. Gabe, L. Hughes, F. L. Lee, L. Prasad, K. U. Ingold, *J. Am. Chem. Soc.* **107** (1985) 7053.
4. S. W. Benson, *Thermochemical Kinetics*; Wiley: New York, 1976.
5. G. Wilkinson In *Proceedings of the 5th International Conference on Organometallic Chemistry*, Moscow, 1971; Butterworths: London, 1972.
6. P. J. Davidson, M. F. Lappert, R. Pearce, *Chem. Rev.* **76** (1976) 219.
7. G. Pilcher, *J. Chem. Thermodynamics* **28** (1996) 1195; *Chem. Brit.* **32**, No. 9 (1996) 76.
8. J. C. G. Calado, A. R. Dias, J. A. Martinho Simões, M. A. V. Ribeiro da Silva, *J. Chem. Soc., Chem. Commun.* (1978) 737.
9. J. C. G. Calado, A. R. Dias, J. A. Martinho Simões, M. A. V. Ribeiro da Silva, *J. Organometal. Chem.* **174** (1979) 77.
10. A. R. Dias, J. A. Martinho Simões, *Polyhedron* **7** (1988) 1531.
11. J. A. Martinho Simões, J. L. Beauchamp, *Chem. Rev.* **90** (1990) 629.
12. J. A. Martinho Simões, *NIST Organometallic Database*, to be released.
13. J. B. Pedley, *Thermochemical Data and Structures of Organic Compounds*; TRC Data Series, Vol. I; Thermodynamics Research Center: College Station, 1994.
14. W. G. Mallard, General Editor *NIST Chemistry WebBook* (<http://webbook.nist.gov/chemistry>); NIST Standard Reference Database 69-February 1997 Release.
15. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, A. N. Syverud, *JANAF Thermochemical Tables* (3rd ed.); *J. Phys. Chem. Ref. Data* **14** (1985), Suppl. No. 1.
16. D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schumm, I. Halow, S. M. Bailey, K. L. Chumey, R. L. Nuttall, *The NBS Tables of Chemical Thermodynamic Properties*; *J. Phys. Chem. Ref. Data* **11** (1982), Suppl. No. 2.
17. J. D. Cox, G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970.
18. J. A. Martinho Simões, M. E. Minas da Piedade, In *Energetics of Organic Radicals*; J. A. Martinho Simões, A. Greenberg, J. F. Liebman, Eds.; SEARCH Series, Vol. 4; Blackie: London, 1996; Chapter 6.
19. G. C. Vogel, R. S. Drago, *J. Chem. Ed.* **73** (1996) 701, and references cited therein.
20. Y.-R. Luo, S. W. Benson, *Acc. Chem. Res.* **25** (1992) 375, and references cited therein.
21. See, for example, *The Chemical Bond, Structure and Dynamics*; A. Zewail, Ed.; Academic Press: San Diego, 1992.
22. See, for example, R. H. Crabtree, *The Organometallic Chemistry of the Transition Metals* (2nd ed.); Wiley: New York, 1994.
23. J. W. Bruno, T. J. Marks, L. R. Morss, *J. Am. Chem. Soc.* **105** (1983) 6824.
24. J. W. Bruno, H. A. Stecher, L. R. Morss, D. C. Sonnenberger, T. J. Marks, *J. Am. Chem. Soc.* **108** (1986) 7275.
25. L. E. Schock, T. J. Marks, *J. Am. Chem. Soc.* **110** (1988) 7701.
26. M. J. Calhorda, A. R. Dias, M. E. Minas da Piedade, M. S. Salema, J. A. Martinho Simões, *Organometallics* **6** (1987) 734.
27. M. J. Calhorda, M. A. A. F. de C. T. Carrondo, A. R. Dias, A. M. Galvão, M. H. Garcia, A. M. Martins, M. E. Minas da Piedade, C. I. Pinheiro, C. C. Romão, J. A. Martinho Simões, L. F. Veiros, *Organometallics* **10** (1991) 483.
28. S. P. Nolan, R. Lopez de la Vega, C. D. Hoff, *J. Organometal. Chem.* **315** (1986) 187.
29. S. P. Nolan, R. Lopez de la Vega, S. L. Mukerjee, A. A. Gonzalez, K. Zhang, C. D. Hoff, *Polyhedron* **7** (1988) 1491.
30. S. P. Nolan, R. Lopez de la Vega, S. L. Mukerjee, C. D. Hoff, *Inorg. Chem.* **25** (1986) 1160.
31. J. A. Connor, M. T. Zafarani-Moattar, J. Bickerton, N. I. El Saied, S. Suradi, R. Carson, G. Al-Takhin, H. A. Skinner, *Organometallics* **1** (1982) 1166.
32. B. B. Wayland, in *Energetics of Organometallic Species*; J. A. Martinho Simões, Ed.; Kluwer: Dordrecht, 1992; p 69.
33. G. Yoneda, D. M. Blake, *J. Organometal. Chem.* **190** (1980) C71.
34. G. Yoneda, D. M. Blake, *Inorg. Chem.* **20** (1981) 67.
35. C. T. Mortimer, *Rev. Inorg. Chem.* **6** (1984) 233.
36. R. L. Brainard, G. M. Whitesides, *Organometallics* **4** (1985) 1550.
37. H. P. Diogo, J. A. Simoni, M. E. Minas da Piedade, A. R. Dias, J. A. Martinho Simões, *J. Am. Chem. Soc.* **115** (1993) 2764.
38. A. A. Gonzalez, C. D. Hoff, *Inorg. Chem.* **28** (1989) 4295.
39. M. E. Minas da Piedade, J. A. Martinho Simões, *J. Organometal. Chem.* **518** (1996) 167.
40. D. R. Stull, E. F. Westrum, Jr., G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*; Wiley: New York, 1969.
41. J. P. Leal, A. Pires de Matos, J. A. Martinho Simões, *J. Organometal. Chem.* **403** (1991) 1.
42. J. P. Leal, J. A. Martinho Simões, *J. Organometal. Chem.* **460** (1993) 131.
43. a) J. P. Leal, P. M. Nunes, M. E. Minas da Piedade, to be published. b) T. Barreira, J. P. Leal, to be published.
44. A. R. Dias, J. A. Martinho Simões, C. Teixeira, C. Airoldi, A. P. Chagas, *J. Organometal. Chem.* **335** (1987) 71.
45. A. R. Dias, J. A. Martinho Simões, C. Teixeira, C. Airoldi, A. P. Chagas, *J. Organometal. Chem.* **361** (1989) 319.
46. D. Griller, J. A. Martinho Simões, D. D. M. Wayner, In *Sulfur-Centered Reactive Intermediates in Chemistry and Biology*; C. Chatgililoglu, K.-D. Asmus, Eds.; Plenum: New York, 1991.
47. A. R. Dias, J. A. Martinho Simões, C. Teixeira, C. Airoldi, A. P. Chagas, *Polyhedron* **10** (1991) 1433.
48. J. A. Martinho Simões, In *Energetics of Organometallic Species*; J. A. Martinho Simões, Ed.; NATO ASI Series C No. 367; Kluwer: Dordrecht, 1992.
49. J. P. Leal, J. A. Martinho Simões, *Organometallics* **12** (1993) 1442.
50. P. B. Dias, M. E. Minas da Piedade, J. A. Martinho Simões, *Coord. Chem. Rev.* **135/136** (1994) 737.
51. J. F. Liebman, J. A. Martinho Simões, S. W. Slayden, In *Lithium Chemistry: Principles and Applications*; P. von R. Schleyer, A.-M. Sapse, Eds.; Wiley: New York, 1995.
52. J. F. Liebman, J. A. Martinho Simões, S. W. Slayden, In *The Chemistry of Organic Arsenic, Antimony and Bismuth Compounds*; S. Patai, Ed.; Wiley: New York, 1994.
53. J. F. Liebman, J. A. Martinho Simões, S. W. Slayden, In *The Chemistry of Organic Germanium, Tin, and Lead Compounds*; S. Patai, Ed.; Wiley: New York, 1995.
54. J. F. Liebman, J. A. Martinho Simões, S. W. Slayden, *Struct. Chem.* **6** (1995) 65.
55. M. Sana, G. Leroy, C. Wilante, *Organometallics* **10** (1991) 264.
56. See, for example, J. Baggot, *Perfect Symmetry*; Oxford University Press: Oxford, 1996.
57. H. W. Kroto, J. R. Heath, J. R. O'Brien, S. C. Curl, R. Smalley, *Nature* **318** (1985) 162.
58. W. Krätschmer, L. D. Lamb, K. Fostiropoulos, D. R. Huffman, *Nature* **347** (1990) 354.

59. For a leading reference see M. S. Dresselhaus, G. Dresselhaus, P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, 1996.
60. H. P. Diogo, M. E. Minas da Piedade, T. J. S. Dennis, J. P. Hare, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc., Faraday Trans* **89** (1993) 3541.
61. H. P. Diogo, M. E. Minas da Piedade, A. D. Darwish, T. J. S. Dennis, *J. Phys. Chem* **58** (1997) 1465.
62. V. Piacente, G. Gigli, P. Scardala, A. Giustini, D. Ferro, *J. Phys. Chem.* **99** (1995) 14052.
63. (a) T. Kiyobayashi, M. Sakiyama, *Annual Report of Microcalorimetry Research Center, Faculty of Science, Osaka University*, **13** (1992) 58; (b) T. Kiyobayashi, M. Sakiyama, *Fullerene Sci. Technol.* **1** (1993) 269.
64. H.-D. Beckhaus, S. Verevkin, C. Rüchardt, F. Diederich, C. Thilgen, U.-H. ter Meer, H. Mohn, W. Müller, C. S. Foote, *Angew. Chem. Int. Ed. Engl.* **33** (1994) 996.
65. H.-D. Beckhaus, C. Rüchardt, M. Kao, F. Diederich, C. S. Foote, *Angew. Chem. Int. Ed. Engl.* **31** (1992) 63. We have recalculated the uncertainty reported by these authors in order to include the error from the enthalpy of formation of gaseous CO<sub>2</sub>.
66. W. V. Steele, R. D. Chirico, N. K. Smith, W. E. Billups, P. R. Elmore, A. E. Wheeler, *J. Phys. Chem.* **96** (1992) 4731.
67. V. P. Kolesov, S. M. Pimenova, V. K. Pavlovich, N. B. Tamm, A. A. Kurskaya, *J. Chem. Thermodynamics* **28** (1996) 1121.
68. A. Xu-wu, H. Jun, B. Zheng, *J. Chem. Thermodynamics* **28** (1996) 1115.
69. J. M. Rudzinski, Z. Slanina, M. Togasi, E. Ōsawa, T. Iizuka, *Thermochim. Acta* **125** (1988) 155.
70. M. Froimowitz, *J. Comp. Chem.* **12** (1991) 1129.
71. J. Almlöf, H. P. Lüthi, *Supercomputer Research in Chemistry and Chemical Engineering*; ACS Symposium Series 353; American Chemical Society: Washington, 1987.
72. S. Tseng, M.-Y. Shen, C.-H. Yu, *Theoret. Chim. Acta* **92** (1995) 269.
73. (a) B. L. Zhang, C. Z. Wang, K. M. Ho, *Chem. Phys. Lett.* **193** (1992) 225. (b) B. L. Zhang, C. Z. Wang, K. M. Ho, C. H. Xu, C. T. Chan, *J. Chem. Phys.* **97** (1992) 5007.
74. R. L. Murry, J. R. Colt, G. E. Scuseria, *J. Phys. Chem.* **97** (1993) 4954.
75. F. Diederich, R. L. Whetten, C. Thilgen, R. Ettl, I. Chao, M. M. Alvarez, *Science* **254** (1991) 1768.
76. J. M. Schulman, R. L. Disch, M. A. Miller, R. C. Peck, *Chem. Phys. Lett.* **141** (1987) 45.
77. J. Cioslowski, *Chem. Phys. Lett.* **216** (1993) 389.
78. D. A. Armitage, C. W. Bird, *Tetrahedron Lett.* **34** (1993) 5811.
79. S. Tseng, C.-H. Yu, *Chem. Phys. Lett.* **231** (1994) 331.
80. J. M. Schulman, R. L. Disch, *J. Chem. Soc., Chem. Commun.* (1991) 411.
81. D. Bakowies, W. Thiel, *J. Am. Chem. Soc.* **113** (1991) 3704.
82. J. M. Schulman, R. C. Peck, R. L. Disch, *J. Am. Chem. Soc.* **111** (1989) 5675.
83. N. Matsuzawa, D. A. Dixon, *J. Phys. Chem.* **96** (1992) 6241.
84. E. Roduner, I. D. Reid, *Chem. Phys. Lett.* **223** (1994) 149.
85. M. D. Newton, R. E. Stanton, *J. Am. Chem. Soc.* **108** (1986) 2469.
86. M. Manoharan, M. M. Balakrishnarajan, P. Venuvanalingam, K. Balasubramanian, *Chem. Phys. Lett.* **222** (1994) 95.
87. M. Kolb, W. Thiel, *J. Comp. Chem.* **14** (1993) 37.
88. D. S. Marynick, S. K. Estreicher, *Chem. Phys. Lett.* **132** (1986) 383.
89. J. Cioslowski, *Electronic Structure and Calculations on Fullerenes and their Derivatives*; Oxford University Press: Oxford, 1995.
90. CODATA Key Values for Thermodynamics; J. D. Cox, D. D. Wagman, V. A. Medvedev, Eds.; Hemisphere: New York, 1989.
91. For a leading reference see, J. Cadet, P. Vigny, *Bioorganic Photochemistry*; H. Morrison Ed.; Wiley: New York, 1990; Vol. 1, p 1.
92. See, for example, G. M. Myles, A. Sancar, *Chem. Res. Toxicol.* **2** (1989) 197.
93. H. P. Diogo, A. R. Dias, A. Dhalla, M. E. Minas da Piedade, T. P. Begley, *J. Org. Chem.* **56** (1991) 7340.
94. P.B. Dias, C. Teixeira, A.R. Dias, J.A. Simoni, J.A. Martinho Simões, *J. Organometal. Chem.* **482** (1994) 111.