*J. Phys. Chem. A* **2006,** *110,* 299−302

# Comparative Studies of Hyperhomodesmotic Reactions for the Calculation of Standard Heats of Formation of Fullerenes

**Cheng H. Sun,[†] Gao Q. Lu,*[‡,§] and Hui M. Cheng*[†,⊥]**

*Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, 72 Wenhua Road, Shenyang 110016, China, and ARC Center for Functional Nanomaterials, School of Engineering, University of Queensland, Brisbane, QLD 4072, Australia*

*Received: August 25, 2005; In Final Form: November 3, 2005*

How can the accuracy of the calculated standard heats of formation $\Delta H_f^0$ of fullerenes be improved? How reliable are the values of $\Delta H_f^0$ calculated from hyperhomodesmotic reactions? This work is the first to address these questions. By comparing the results obtained from three hyperhomodesmotic reactions containing only fullerenes, it is illustrated that both the resonance contribution and the strain energy contribution should be considered in the construction of hyperhomodesmotic reactions. An attempt to construct such hyperhomodesmotic reactions for fullerenes has been carried out, and several new insights are indicated.

## 1. Introduction

The standard heats of formation $\Delta H_f^0$ can be obtained by ab initio calculations based upon the calculation of the enthalpy change of a hypothetical reaction; however, the limitation of this method is that the accuracy of such calculated results strongly depends on the experimental data and reactions employed.[1] Therefore, the accuracy of a calculated $\Delta H_f^0$ is determined mainly by two factors, (1) the accuracy of experimental data and (2) the suitability of the hypothetical reactions. Therefore, to obtain an accurate $\Delta H_f^0$, employed experimental values of $\Delta H_f^0$ for reference molecules are expected to be as precise as possible. Also to provide a more extensive error cancellation, more and more exact terms are added for the construction of hypothetical reactions, which include isodesmic,[2] homodesmotic,[3] and hyperhomodesmotic reactions.[4]

The values of $\Delta H_f^0$ of fullerenes, which are fundamentally important for both calorimetric measurements and other theoretical studies,[5] have been calculated by several groups using different approaches.[5−8] A basic question about these methods is the accuracy of these calculations. It has been found that even hyperhomodesmotic reactions are not always reliable for molecules with strong resonance of $\pi$ electrons and strain energies,[9] such as polycyclic aromatic hydrocarbons (PAHs). Hence, Schulman et al. suggested that hyperhomodesmotic reactions containing only aromatic species may partly cancel this error, due to partly considering the resonance in reactants and products.[9] A total of 16 PAHs were investigated based on this idea, and accurate results were obtained even at the low level of STO-3G, suggesting the validity of this restriction,[9] which has been taken into account in the investigation of other PAHs and fullerenes.[5,10,11] For instance, Cioslowski et al.[5] systematically investigated this issue at the B3LYP/6-31G(d) level of theory based on the hypothetical reaction

$$(N/60)C_{60} \rightarrow C_N \qquad (1)$$

In contrast to planar PAHs, however, fullerenes have strong strain energy ($E_S$), which has a significant effect on their stabilities.[5,10,12] Hence, the consideration of strain energies in the calculation of $\Delta H_f^0$ for fullerenes may yield an improvement similar to Schulman's success. As can be seen, although reaction 1 ($R_1$, as described by eq 1) is a hyperhomodesmotic reaction only containing fullerenes, the strain energies ($E_S$) in products and reactants are not as yet considered. Therefore, to approach more accurate values of $\Delta H_f^0$ for fullerenes, $R_1$ should be improved.

Conventional hyperhomodesmotic reactions[4] cancel out the additive contribution; hyperhomodesmotic reactions containing only aromatic species proposed by Schulman et al.[9] cancel out both the additive contribution and the resonance contribution. However, it is necessary to point out that the consideration of the resonance contribution in this way is qualitative since the resonance energies contributed by all aromatic species are not balanced quantitatively. As an improvement, if the contribution due to the strain energy of the reactants in the hyperhomodesmotic reaction matched that of the products, both the resonance and the strain energies would be considered simultaneously. The difficulty is that experimental data of $\Delta H_f^0$ must be available for all reference molecules. At the current stage, however, only the experimental standard heats of formation for $C_{60}$ and $C_{70}$ are available; hence, for fullerenes, there is no alternative but to use $C_{60}$ and $C_{70}$ for consideration of the above requirements. The question is whether it is necessary to consider the contributions due to the resonance and strain energy in the construction of hyperhomodesmotic reactions, and, if so, how is one to realize it? Also, is it possible to construct such reactions using only $C_{60}$ and $C_{70}$ for any fullerenes and what about the reliability and accuracy of the values of $\Delta H_f^0$ calculated from such reactions?

The present work is the first to address these issues. First, three different hyperhomodesmotic reactions using only $C_{60}$ and $C_{70}$ are constructed and the standard heats of formation of 114 isolated pentagon rule (IPR) fullerenes are calculated based on the above reactions and compared with each other. Second,

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[†] Chinese Academy of Sciences.

[‡] University of Queensland.

[§] E-mail: maxlu@uq.edu.au.

[⊥] E-mail: cheng@imr.ac.cn.

10.1021/jp054823s CCC: $33.50

based on the calculated data, the effects of the uncertainties of experimental data and unbalanced strain energies on the calculation of $\Delta H_f^0$ of fullerenes are discussed. Moreover, in the hyperhomodesmotic reactions proposed in the present work, both the resonance and the strain energies are considered using only $C_{60}$ and $C_{70}$ for any fullerenes.

## 2. Hyperhomodesmotic Reactions and Computational Methods

For fullerenes, there are two kinds of bonds, C=C (α) and C−C (λ), according to the classic valence-bond theory. Moreover, it can be seen,[13] $N_C = 2\kappa_\alpha = \kappa_\lambda$, where $N_C$, $\kappa_\alpha$, and $\kappa_\lambda$ are the numbers of carbon atoms, bonds of α and λ, respectively. This relationship suggests that the number of bonds in products and reactants naturally matches with each other when the number of carbon atoms is balanced. Therefore, all reactions only involving fullerenes must be hyperhomodesmotic reactions. Using $C_{60}$ and $C_{70}$, there are two other reactions in addition to $R_1$:

$$(N/70)C_{70} \rightarrow C_N \tag{2}$$

$$xC_{60} + yC_{70} \rightarrow C_N \tag{3}$$

For eq 3

$$60x + 70y = N \tag{4}$$

Equation 4 is an indefinite equation, suggesting that it is possible to adjust $x$ and $y$ in order to satisfy other conditions. To consider the strain energy contribution as illustrated above, the strain energies in reactants and products are balanced:

$$xE_S^{C_{60}} + yE_S^{C_{70}} = E_S^{C_N} \tag{5}$$

where $E_S^{C_{60}}$, $E_S^{C_{70}}$ and $E_S^{C_N}$ denote the strain energies of $C_{60}$, $C_{70}$, and $C_N$, respectively. On the basis of eqs 4 and 5, $x = (70E_S^{C_N} - NE_S^{C_{70}})/(70E_S^{C_{60}} - 60E_S^{C_{70}})$, $y = (60E_S^{C_N} - NE_S^{C_{60}})/(60E_S^{C_{70}} - 70E_S^{C_{60}})$. Until now, a hyperhomodesmotic reaction with balanced strain energies has been constructed using only $C_{60}$ and $C_{70}$ for $C_{N.}$ So far, three hyperhomodesmotic reactions for fullerenes, eq 1 as reaction 1 ($R_1$), eq 2 as reaction 2 ($R_2$) and eq 3 as reaction 3 ($R_3$), have been constructed. Strain energies in the products and reactants for $R_1$ and $R_2$ are unbalanced, but they are balanced for $R_3$.

The difficulty for $R_3$ is the determination of the strain energies of the reactants and products. Normally strain energies are defined relative to some standard structures. When structural parameters deviate from the standard values, strain energies are introduced, which can be defined based on the types of structural distortions, such as, for fullerenes, $E_{np}$ and $E_{ba}$ for strain energies due to nonplanar distortions and bond-angle bending away from the sp$^2$ ideal, respectively. For fullerenes, it is still difficult to calculate all terms of strain energies due to the shortage of force constants. Considering that $E_{np}$ and $E_{ba}$ have been identified as two major sources of destabilization in a study of large carbon clusters, $E_S$ in the eq 5 is approximated expressed by the sum of $E_{np}$ and $E_{ba}$, $E_S \approx E_{ba} + E_{np}$. Details about these calculations of $E_{np}$ and $E_{ba}$ can be found elsewhere.[10,14−16] The above assumption is thought to be reasonable due to two facts: (i) other terms of strain energies are small compared with $E_{ba} + E_{np}$. For instance, the total strain energy for $C_{60}$ was estimated to be ∼100% of $\Delta H_f^0$ and $E_{np}$ to be 77% of the total strain energy.[10,15] (ii) Without considering the strain energy contribution, the standard heats of formation of planar PAHs were calculated accurately by Schulman et al.,[9] which suggested that strain energies can be ignored when $E_{np}$ is not significant.

## 3. Results and Discussion

Table 1 presents the values of $E_S$ for 114 IPR fullerenes. Using the data for the total energies of fullerenes from Cioslowski et al.,[5] $\Delta H_f^0$ was recalculated based on $R_1$, $R_2$, and $R_3$, as listed in Table 1. The experimental values of $\Delta H_f^0(C_{60})$ and $\Delta H_f^0(C_{70})$ are 604.6 and 658.5 kcal/mol,[11] respectively. The effect of the employed experimental results on the calculations may be discussed as follows. As seen in Table 1, it was found that, $\Delta H_{f1}^0 < \Delta H_{f2}^0 < \Delta H_{f3}^0$. The subscripts denote the hyperhomodesmotic reaction involved. The difference between $\Delta H_{f1}^0$ and $\Delta H_{f3}^0$ ranged from 9.2 kcal/mol for $C_{72}(D_{6d})$ to 63.8 kcal/mol for $C_{102}(C_1)$. Moreover, the difference increased steadily with the increasing number of carbon atoms. Although no further experimental data are available to indicate which one is more accurate, it is necessary to recognize that the calculated $\Delta H_f^0$ could contain errors of the order of tens of kilocalories per mole, though all reactions employed here ($R_1$, $R_2$, and $R_3$) are hyperhomodesmotic reactions containing only fullerenes. Therefore, calculations based on these reactions are not necessarily as accurate as that obtained by Schulman et al.[9] in planar PAHs since fullerenes have high strain energies, which are not found in planar PAHs.

From Table 1, it can be seen that the values of $\Delta H_f^0$ calculated from hyperhomodesmotic reactions as defined by Schulman et al.[9] present significant uncertainty. Thus, it is necessary to investigate the source of this uncertainty and to further consider the suitability of the above hyperhomodesmotic reactions. There is no doubt that uncertainties in experimental data can have a significant effect on the calculations of $\Delta H_f^0$, which should be investigated before discussing the effect of unbalanced strain energies on the calculation of $\Delta H_f^0$. In fact, experimental data for $\Delta H_f^0(C_{60})$ and $\Delta H_f^0(C_{70})$ in the literature vary remarkably, from 599.1 to 634.9 kcal/mol for $\Delta H_f^0(C_{60})$ and from 633.8 to 666.3 kcal/mol for $\Delta H_f^0(C_{70})$.[11] Therefore, it is necessary to consider the differences among the values of $\Delta H_f^0$ calculated from $R_1$, $R_2$, and $R_3$ when different experimental data are employed for same reference molecules. Mathematically, the three reactions have slight differences if $R_1$ can produce an accurate $\Delta H_f^0(C_{70})$ from the experimental value of $\Delta H_f^0(C_{60})$ or $R_2$ can produce an accurate $\Delta H_f^0(C_{60})$ from the experimental value of $\Delta H_f^0(C_{70})$. For instance, based on $R_1$, $^{70}/_{60}C_{60} \rightarrow C_{70}$; hence, $R_2$ can be written as, $(N/70)(^{70}/_{60}C_{60}) \rightarrow C_N$, and $R_3$ can be written as, $xC_{60} + y(^{70}/_{60}C_{60}) \rightarrow C_N$, and these expressions are equal to $R_1$. This result suggests that if $\Delta H_f^0(C_{70})$ produced by $R_1$ is close to the experimental $\Delta H_f^0(C_{70})$ employed in $R_2$ and $R_3$, data of $\Delta H_f^0$ calculated from $R_1$, $R_2$, and $R_3$ will be close to each other. Using currently available data for $\Delta H_f^0(C_{60})$ and $\Delta H_f^0(C_{70})$, $\Delta H_f^0(C_{70})$ is calculated from $R_1$: (**599.1**, 635.5), (**599.4**, 635.9), (**604.6**, 642.0), (**618.6**, 658.3) and (**634.9**, 677.3). $\Delta H_f^0(C_{60})$ is calculated from $R_2$: (597.6, **633.8**), (618.8, **658.5**), (625.5, **666.3**), in units of kcal/mol. The bold numbers in parentheses are experimental data from the Supporting Information from ref 11 and the literature cited in it, and the others were calculated based on the bold ones. Cioslowski et al.[5] have taken the value of 618.1 ± 3.4 kcal/mol for $\Delta H_f^0(C_{60})$ and produced 657.7 kcal/mol for $\Delta H_f^0(C_{70})$, which is close to (618.8, **658.5**), suggesting that $R_1$, $R_2$, and $R_3$ have no remarkable difference in this case. However, according to the data given by the CRC handbook,[17] $\Delta H_f^0(C_{60}) = 598.6$ kcal/mol and $\Delta H_f^0(C_{70}) = 659.1$ kcal/mol, $R_1$, $R_2$, and $R_3$ will have remarkable differences. Hence, accurate experimental data of

**TABLE 1: Strain Energies and Standard Heats of Formation of 114 IPR Fullerenes Based on $R_1$, $R_2$, and $R_3$[a]**

| IPR(sym) | $E_S$ | $\Delta H_{f1}^0$ | $\Delta H_{f2}^0$ | $\Delta H_{f3}^0$ | IPR(sym) | $E_S$ | $\Delta H_{f1}^0$ | $\Delta H_{f2}^0$ | $\Delta H_{f3}^0$ |
|---|---|---|---|---|---|---|---|---|---|
| $C_{60}(I_h)$ | 636.6 | **604.6** | 618.8 | **604.6** | $C_{84}(C_2)$ | 668.6 | 723.9 | 743.8 | 764.5 |
| $C_{70}(D_{5h})$ | 652.0 | 642.0 | **658.5** | **658.5** | $C_{84}(C_s)$ | 665.6 | 726.2 | 746.1 | 767.4 |
| $C_{72}(D_{6d})$ | 680.0 | 688.6 | 705.6 | 703.9 | $C_{84}(C_2)$ | 669.0 | 705.8 | 725.7 | 746.4 |
| $C_{74}(D_{3h})$ | 653.1 | 678.0 | 695.4 | 702.0 | $C_{84}(C_1)$ | 665.5 | 709.8 | 729.7 | 751.0 |
| $C_{76}(D_2)$ | 667.8 | 682.0 | 700.0 | 707.3 | $C_{84}(C_2)$ | 667.9 | 722.3 | 742.2 | 763.1 |
| $C_{78}(D_3)$ | 671.9 | 695.0 | 713.4 | 723.4 | $C_{84}(C_s)$ | 676.2 | 712.6 | 732.5 | 751.8 |
| $C_{78}(C_{2v})$ | 671.2 | 691.7 | 710.1 | 720.2 | $C_{84}(C_s)$ | 665.9 | 708.8 | 728.7 | 749.9 |
| $C_{78}(C_{2v})$ | 660.3 | 685.1 | 703.5 | 715.6 | $C_{84}(C_s)$ | 670.2 | 705.5 | 725.4 | 745.8 |
| $C_{78}(D_{3h})$ | 685.9 | 709.7 | 728.1 | 735.5 | $C_{84}(C_{2v})$ | 672.2 | 719.2 | 739.1 | 759.2 |
| $C_{78}(D_{3h})$ | 651.9 | 689.6 | 708.0 | 721.6 | $C_{84}(C_{2v})$ | 677.0 | 713.2 | 733.1 | 752.3 |
| $C_{80}(D_{5d})$ | 675.8 | 709.2 | 728.1 | 740.8 | $C_{84}(D_{3d})$ | 668.6 | 707.8 | 727.7 | 748.4 |
| $C_{80}(D_2)$ | 676.3 | 706.6 | 725.5 | 738.1 | $C_{84}(\mathrm{T_d})$ | 690.7 | 728.2 | 748.1 | 764.8 |
| $C_{80}(C_{2v})$ | 665.0 | 713.3 | 732.2 | 746.8 | $C_{84}(D_2)$ | 662.2 | 713.8 | 733.7 | 755.6 |
| $C_{80}(D_3)$ | 672.4 | 715.6 | 734.5 | 747.8 | $C_{84}(D_2)$ | 663.2 | 697.8 | 717.7 | 739.4 |
| $C_{80}(C_{2v})$ | 657.6 | 714.9 | 733.8 | 749.8 | $C_{84}(D_{2d})$ | 663.4 | 697.5 | 717.4 | 739.1 |
| $C_{82}(C_2)$ | 674.1 | 709.4 | 728.7 | 745.1 | $C_{84}(D_{6h})$ | 671.0 | 704.7 | 724.6 | 744.9 |
| $C_{82}(C_s)$ | 676.7 | 708.4 | 727.7 | 743.6 | $C_{86}(C_1)$ | 688.6 | 742.3 | 762.6 | 783.1 |
| $C_{82}(C_2)$ | 670.0 | 701.7 | 721.0 | 738.1 | $C_{86}(C_2)$ | 697.1 | 743.3 | 763.6 | 782.5 |
| $C_{82}(C_s)$ | 667.2 | 705.6 | 724.9 | 742.6 | $C_{86}(C_2)$ | 684.1 | 734.6 | 754.9 | 776.2 |
| $C_{82}(C_2)$ | 663.4 | 710.0 | 729.3 | 747.7 | $C_{86}(C_2)$ | 681.2 | 737.4 | 757.7 | 779.5 |
| $C_{82}(C_s)$ | 659.6 | 713.9 | 733.2 | 752.2 | $C_{86}(C_1)$ | 676.9 | 736.4 | 756.7 | 779.3 |
| $C_{82}(C_{3v})$ | 658.5 | 732.4 | 751.7 | 770.9 | $C_{86}(C_2)$ | 679.7 | 731.4 | 751.7 | 773.8 |
| $C_{82}(C_{2v})$ | 655.9 | 720.0 | 739.3 | 759.0 | $C_{86}(C_1)$ | 676.1 | 740.5 | 760.8 | 783.6 |
| $C_{84}(D_2)$ | 709.5 | 749.2 | 769.1 | 782.4 | $C_{86}(C_s)$ | 668.7 | 750.8 | 771.1 | 778.2 |
| $C_{84}(C_2)$ | 692.0 | 730.7 | 750.6 | 767.1 | $C_{86}(C_{2v})$ | 671.0 | 756.9 | 777.2 | 800.9 |
| $C_{84}(C_s)$ | 692.0 | 729.7 | 749.6 | 766.1 | $C_{86}(C_{2v})$ | 677.5 | 734.2 | 754.5 | 777.0 |
| $C_{84}(D_{2d})$ | 677.0 | 712.4 | 732.3 | 751.5 | $C_{86}(C_1)$ | 673.1 | 726.5 | 746.8 | 770.1 |
| $C_{84}(D_2)$ | 675.3 | 713.5 | 733.4 | 752.9 | $C_{86}(C_1)$ | 673.2 | 726.4 | 746.7 | 770.0 |
| $C_{84}(C_{2v})$ | 674.6 | 714.8 | 734.7 | 754.3 | $C_{86}(C_1)$ | 669.7 | 734.1 | 754.4 | 778.3 |
| $C_{84}(C_{2v})$ | 668.0 | 722.2 | 742.1 | 762.9 | $C_{86}(C_2)$ | 672.7 | 743.0 | 763.3 | 786.7 |
| $C_{84}(C_2)$ | 669.0 | 719.6 | 739.5 | 760.2 | $C_{86}(C_s)$ | 669.5 | 746.4 | 766.7 | 790.7 |
| $C_{86}(C_s)$ | 680.5 | 726.1 | 746.4 | 768.4 | $C_{92}(D_2)$ | 679.7 | 736.8 | 758.6 | 790.9 |
| $C_{86}(C_2)$ | 673.1 | 714.6 | 734.9 | 758.2 | $C_{94}(C_s)$ | 724.9 | 818.2 | 840.4 | 867.9 |
| $C_{86}(C_3)$ | 675.4 | 735.6 | 755.9 | 778.8 | $C_{94}(C_{2v})$ | 702.1 | 791.9 | 814.1 | 845.7 |
| $C_{86}(D_3)$ | 665.6 | 750.7 | 771.0 | 795.7 | $C_{96}(D_{3h})$ | 768.9 | 856.7 | 879.4 | 902.3 |
| $C_{88}(D_2)$ | 723.5 | 778.9 | 799.7 | 817.3 | $C_{96}(C_{2v})$ | 742.3 | 826.5 | 849.2 | 876.9 |
| $C_{88}(C_1)$ | 697.1 | 745.4 | 766.2 | 788.6 | $C_{96}(D_{2h})$ | 741.3 | 824.7 | 847.4 | 875.3 |
| $C_{88}(C_s)$ | 691.3 | 758.3 | 779.1 | 802.5 | $C_{96}(C_{2v})$ | 718.6 | 798.5 | 821.2 | 853.2 |
| $C_{88}(C_{2v})$ | 694.2 | 740.9 | 761.7 | 784.6 | $C_{96}(D_{6h})$ | 697.1 | 773.2 | 795.9 | 831.9 |
| $C_{88}(C_2)$ | 680.2 | 727.9 | 748.7 | 774.2 | $C_{98}(C_s)$ | 703.5 | 800.0 | 823.1 | 861.3 |
| $C_{88}(C_{2v})$ | 695.0 | 740.9 | 761.7 | 784.5 | $C_{98}(C_s)$ | 725.1 | 814.7 | 837.8 | 872.1 |
| $C_{88}(C_s)$ | 678.1 | 749.3 | 770.1 | 795.9 | $C_{100}(D_2)$ | 687.5 | 772.3 | 795.9 | 840.5 |
| $C_{90}(D_{5h})$ | 702.2 | 743.5 | 764.7 | 789.6 | $C_{100}(D_2)$ | 687.6 | 771.4 | 795.0 | 839.5 |
| $C_{90}(C_{2v})$ | 713.3 | 763.8 | 785.0 | 807.8 | $C_{102}(C_1)$ | 689.6 | 787.7 | 811.8 | 859.3 |
| $C_{90}(C_1)$ | 702.4 | 755.1 | 776.3 | 801.1 | $C_{102}(C_1)$ | 689.0 | 786.1 | 810.2 | 857.8 |
| $C_{90}(C_2)$ | 692.7 | 746.5 | 767.7 | 794.3 | $C_{102}(C_1)$ | 724.7 | 815.4 | 839.5 | 880.6 |
| $C_{90}(C_s)$ | 694.4 | 757.3 | 778.5 | 804.8 | $C_{102}(C_1)$ | 724.6 | 794.1 | 818.2 | 859.3 |
| $C_{90}(C_2)$ | 689.7 | 745.5 | 766.7 | 793.8 | $C_{102}(C_1)$ | 719.9 | 788.7 | 812.8 | 854.8 |
| $C_{92}(C_s)$ | 696.6 | 755.6 | 777.4 | 806.6 | $C_{102}(C_1)$ | 756.0 | 816.4 | 840.5 | 875.9 |
| $C_{92}(C_s)$ | 697.2 | 776.5 | 798.3 | 827.4 | $C_{102}(C_1)$ | 734.8 | 797.6 | 821.7 | 860.9 |
| $C_{92}(C_s)$ | 713.8 | 779.1 | 800.9 | 827.0 | $C_{102}(C_1)$ | 740.6 | 800.9 | 825.0 | 863.2 |
| $C_{92}(C_{2v})$ | 718.8 | 806.0 | 827.8 | 853.0 | $C_{102}(C_{2v})$ | 726.3 | 792.5 | 816.6 | 857.4 |
| $C_{92}(C_2)$ | 703.3 | 781.0 | 802.6 | 830.8 | $C_{102}(C_{2v})$ | 771.7 | 829.3 | 853.4 | 885.9 |
| $C_{92}(D_{2h})$ | 709.9 | 789.8 | 811.6 | 838.4 | $C_{102}(C_s)$ | 738.6 | 804.6 | 828.7 | 867.3 |
| $C_{92}(C_{2v})$ | 696.6 | 782.8 | 804.6 | 833.8 | $C_{102}(C_s)$ | 742.3 | 804.1 | 828.2 | 866.1 |
| $C_{92}(C_s)$ | 693.4 | 758.0 | 779.8 | 809.6 | $C_{102}(C_s)$ | 749.8 | 810.5 | 834.6 | 871.1 |
| $C_{92}(D_2)$ | 669.5 | 740.4 | 762.2 | 796.4 | $C_{102}(D_3)$ | 723.6 | 783.2 | 807.3 | 848.6 |

[a] The bold numbers are experimental data of $\Delta H_f^0(C_{60})$ and $\Delta H_f^0(C_{70})$ employed here. $E_S$, $\Delta H_{f1}^0$, $\Delta H_{f2}^0$, and $\Delta H_{f3}^0$ are in units of kcal/mol.

$\Delta H_f^0(C_{60})$ and $\Delta H_f^0(C_{70})$ could partially answer whether it is reliable to calculate $\Delta H_f^0$ of fullerenes from $R_1$ and $R_2$. Using data from the CRC handbook, results from $R_1$ and $R_2$ are not reliable.

In addition to answer this question based on experimental data, the effect of the unbalanced strain energy $\Delta E_S$ on the calculations of $\Delta H_f^0$ can be discussed theoretically. Figure 1 shows the unbalanced strain energies ($\Delta E_S$) for $R_1$, $R_2$, and $R_3$ vs the number of carbon atoms of 114 IPR fullerenes. Several tendencies can be summarized: (i) both $R_1$ and $R_2$ yield negative unbalanced strain energies; (ii) the changing tendencies of absolute values of $\Delta E_S$ for $R_1$ and $R_2$ are consistent with that

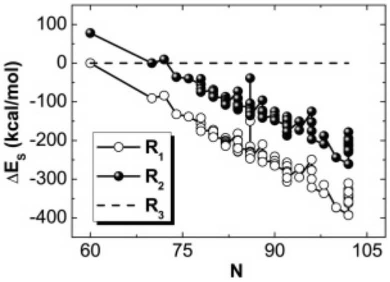

**Figure 1.** Unbalanced strain energies ($\Delta E_S$) for $R_1$, $R_2$, and $R_3$ vs the number of carbon atoms of 114 IPR fullerenes.

of ($\Delta H_{f3}^0 - \Delta H_{f1}^0$) and ($\Delta H_{f3}^0 - \Delta H_{f2}^0$). From Table 1, $\Delta H_{f1}^0 < \Delta H_{f2}^0 < \Delta H_{f3}^0$, it seems that, for the same molecule, the values of $\Delta H_f^0$ calculated from different hyperhomodesmotic reactions increase with the increment of $\Delta E_S$; (iii) it is noticed that, with increasing molecular sizes, $|\Delta E_S|$ increases monotonically in $R_1$ and $R_2$, suggesting that the errors caused by $\Delta E_S$ represent a molecular size effect, which is important for the calculation of fullerenes with hundreds of atoms.

In ref 9, the improvement of the accuracy of the predicted standard heats of formation for PAHs is essentially due to the consideration of the resonance contributions in reactants and products. As an improvement, $R_3$ took the strain energy contribution into account by matching the strain energies in reactants and products, using only $C_{60}$ and $C_{70}$ as reference molecules. However, it is cautiously pointed out that $R_3$ is just one possible approach, and the accuracy of $\Delta H_f^0$ obtained from $R_3$ needs further confirmation by experimental data. The above summarized tendencies are intended to be helpful for the exploration of suitable hyperhomodesmotic reactions for fullerenes. Although it is highly desirable to consider the resonance contribution and the strain energy separately and quantitatively in the construction of hyperhomodesmotic reactions, three reference molecules with experimentally obtainable values of $\Delta H_f^0$ are required. This requirement cannot be satisfied at the current stage. Fortunately, $C_{60}$ and $C_{70}$ species are not the only currently known fullerenes, and isomers of $C_{76}$, $C_{78}$, $C_{80}$, $C_{82}$, and $C_{84}$ have been isolated.[18−20] Hence, more experimental data for $\Delta H_f^0$ may be obtained in the near future, making it possible to explore suitable hyperhomodesmotic reactions by using more fullerenes as reference molecules. Moreover, using these data, the reliability and accuracy of values of $\Delta H_f^0$ calculated from $R_1$, $R_2$, and $R_3$ can be established.

## 4. Conclusions

In conclusion, three hyperhomodesmotic reactions containing only $C_{60}$ and $C_{70}$ have been constructed. Resonance energies are considered in the reactions of $R_1$, $R_2$, and $R_3$, while strain energies are further balanced in the $R_3$ in an approximate way. Using these three reactions, the standard heats of formation for 114 IPR fullerenes were calculated. It was found that the difference among the values of $\Delta H_f^0$ calculated from $R_1$, $R_2$, and $R_3$ can be as large as tens of kilocalories per mole; moreover, $\Delta H_f^0(R_1) < \Delta H_f^0(R_2) < \Delta H_f^0(R_3)$. Thus, it is necessary to investigate the limitation and systematic errors caused by the uncertainties in experimental data and hyperhomodesmotic reactions of fullerenes. Using $R_3$ as an example, it is illustrated that, in the construction of hyperhomodesmotic reactions for fullerenes, it is possible to simultaneously consider the contributions due to resonance and strain energy in reactants and products using only $C_{60}$ and $C_{70}$ as reference molecules.

**Acknowledgment.** We thank Prof. J. Cioslowski for kindly offering the coordinates of IPR fullerenes used in this work and Prof. R. C. Haddon for valuable discussions about the calculation of strain energies of fullerenes and kindly offering the POAV package. The financial support from the Chinese Academy of Sciences' Shenyang Research Centre for Interfacial Materials and the ARC Centre for Functional Nanomaterials, Australia, to this work is acknowledged. This work was also supported by National Science Foundation of China (No. 50328204) and the State Major Fundamental Research Project of MOST (G2000026403).

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