Ring Conserved Isodesmic Reactions: A New Method for Estimating the Heats of Formation of Aromatics and PAHs

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Density functional theory (DFT) has been used along with isodesmic reaction schemes to estimate heats of formation for aromatics and polynuclear aromatic hydrocarbons (PAHs). Calculations have been performed for 42 molecules, 12 of which have uncertain or unknown experimental values, using the B3-LYP functional with the small 6-31G(d) basis set. Heats of formation for the group of test molecules were estimated using both conventional bond separation (BS) isodesmic reactions as well as a new technique of ring conserved (RC) isodesmic reactions which is able to correct systematic errors in B3-LYP calculations. When a ring conserved isodesmic reaction based on delocalization energies is used, the estimated heat of formation is more accurate than that obtained by the bond separation technique. The methodology for creating and using appropriate ring conserved isodesmic reactions is discussed. The present scheme also compares favorably against a recently developed bond centered group additivity scheme that was tested against a large number of PAH molecules.

Introduction

Thermochemical and molecular properties are critical parameters in many aspects of gas kinetics, and the accuracy to which these parameters are determined can greatly affect the determination of a variety of parameters including rate coefficients, rates of heat release, and branching ratios, all of which are critical in the accurate simulation of reactive gas-phase systems. For instance, in the case of C_6H_5 (phenyl) decomposition, recent theoretical and experimental estimates for the heat of formation of *o*-C_6H_4 have lent considerable support for its formation by H atom ejection from a C_6H_5 (phenyl) radical and for this path to be the dominant channel for phenyl decay[1] as opposed to linearization of the phenyl radical or its rupture to form C_4H_3 and C_2H_2. It is essential that values of $\Delta H_f^\circ{}_{298\,K}$ be obtained to an accuracy within 2 kcal/mol for situations where it is not possible or difficult to obtain good experimental data for multichannel reactions or for the estimation of rate coefficients.

In the case of polynuclear aromatic hydrocarbons (PAHs), there are very limited reliable measurements for $\Delta H_f^\circ{}_{298\,K}$ and the majority of the reported data are for species with a maximum of four rings.[2] The difficulty of performing these measurements makes theoretical methods for determining heats of formation for large aromatics and PAHs attractive if the calculations can be performed with sufficient accuracy so as not to introduce excessive errors into subsequent kinetic calculations.

A large body of work involving theoretical estimates of $\Delta H_f^\circ{}_{298\,K}$ has been performed over the past three decades, some of which have been applied to PAHs. For instance, group additivity (GA) schemes developed by Benson and co-workers[3] were used in very early efforts to compare thermochemical parameters for a large number of PAHs.[4,5] The Stein et al.[4] GA scheme was able to predict ΔH_f° for a test set of 11 PAHs with the mean deviation from experimental values being <2 kcal/mol. An evaluation of the GA methods and semiempirical (AM1) and molecular mechanics methods for estimating thermochemical properties by Herndon et al.[6] concluded that a GA scheme incorporating resonance energy parameters could most accurately predict ΔH_f° with mean deviations from experimental ΔH_f° as low as 1.1 kcal/mol for the same test set of 11 PAHs as that of Stein et al.[4] The largest PAH in this test set was perylene, and because of the lack of experimental information on larger cata- and peri-condensed PAHs, Herndon et al.[6] were only able to compare their GA scheme against molecular mechanics predictions of $\Delta H_f^\circ{}_{298\,K}$ with a good degree of agreement for a set of 153 PAHs, with the largest molecule being phenanthro(4,3-g)chrysene ($C_{30}H_{18}$, seven rings). Pope and Howard[7] in an attempt to estimate the properties for a wide range of five- and six-membered-ring PAH species in their fullerene formation mechanism have compared the group additivity scheme they derived to results from semiempirical methods. They concluded that the group additivity scheme was accurate enough for their kinetics calculations.

The development of very fast and affordable computers with large storage/memory capacities has contributed to the rapid development of ab initio methods that are able to increasingly replicate experimental accuracies for molecular properties and kinetics. Peck et al.[8] and later Herndon[9] used Hartree−Fock (HF) theory with small basis sets to estimate ΔH_f° for aromatics and PAHs.[8,9] Peck et al.[8] derived group equivalents on the basis of the zero point corrected total ab initio energy and the corresponding known experimental heat of formation for a training set of nine molecules. These group equivalents were subsequently used to determine the heat of formation for a larger set of 19 molecules. Herndon's[9] method calculated $\Delta H_f^\circ{}_{298\,K}$ from simple equations obtained by multilinear regression analysis that relate the ab initio energies and the number of C and H atoms to the heats of formation. Herndon et al.[10] in a

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more recent work used empirical structural parameters to correlate ab initio predicted energies at the HF, density functional theory (DFT), and MP2 levels of theory to experimental heats of formation for 11 cata- and peri-condensed PAHs.

Higher level theoretical methods that incorporate electron correlation to estimate molecular energies with greater precision have been developed that include the G2,[11] G3,[12] and CBS-Q[13] composite methods, and these methods have been used to estimate heats of formation that have mean absolute deviations (MADs) from the experimental heats of formation of <2 kcal/mol for a large set of common hydrocarbon molecules having as many as six carbon atoms.

These high level methods become very expensive to use for large molecules with several heavy atoms due to time and memory requirements and are at present not suitable for routine application to large systems such as PAHs particularly when it is necessary to obtain thermochemical information for a large number of species. Thus, a method of estimating heats of formation for PAHs that does not require time-consuming calculations and that is usable beyond the test group of species has been developed. The method that we refer to as ring conserved (RC) isodesmic reactions makes use of inexpensive DFT methods to obtain heats of reaction and has been used to accurately estimate heats of formation for molecules as large as 9,10-diphenylanthracene ($C_{26}H_{18}$). The technique and comparisons with other methods are described below.

Estimation of $\Delta H_f{}^\circ{}_{298\,K}$

The enthalpies of formation at 298 K ($\Delta H_f{}^\circ{}_{298\,K}$) were calculated using the procedure outlined by Notario et al.[14] The DFT calculations were performed using the Gaussian98[15] series of programs, and the input structures were generated using CHEM3D,[16] part of the CHEMOFFICE suite of programs. Geometry optimizations are performed using the B3-LYP functional with the small basis set 6-31G(d). After the geometry of each species had been optimized and the energies obtained, frequency calculations were performed at the same level of theory to confirm that the structures obtained were minima on the potential energy surface. This level of theory has been shown to be adequate for obtaining fairly accurate geometries, vibrational frequencies, and zero point energies and has been used for these properties in a variant to the G3 composite method,[12] the G3B3 method.[17]

Reaction Schemes

In principle, if the heat of formation of a species is not known, then it can be obtained from the Hess cycle for a reaction if the heats of formation of all the other species are known and the heat of reaction is known. Thus, all that is required is to construct an appropriate reaction and the simplest possible reaction is to atomize the molecule of interest. However, while atomization reactions can produce reasonably accurate estimates of $\Delta H_f{}^\circ{}_{298\,K}$ for small molecules, the method has been shown to be inaccurate for large molecules, for example, benzene, due to an accumulation of errors even when molecular energies are computed to a high level of precision using a composite method such as G2.[18,19]

An alternative scheme to atomization reactions is to use isodesmic reactions wherein some of the molecular nature of the species of interest is retained in the products. Hehre et al.[20] showed in the early development of ab initio molecular orbital theory the importance of bond separation (BS) isodesmic reactions, which refer to reactions in which the number and type of bonds are retained.

Raghavachari et al.[19] have suggested the use of BS isodesmic reactions to estimate $\Delta H_f{}^\circ{}_{298\,K}$, since the cancellation of errors in electron correlation energy is more complete when calculating ΔH_r in such reaction schemes, and they utilized[21] this method[20] to evaluate $\Delta H_f{}^\circ{}_{298\,K}$ for a large number of small species that were separated into a simple set of nine reference molecules with well characterized experimental heats of formation (uncertainty ~0.1 kcal/mol) using higher level (G2 and G2MP2) methods.

In general, the use of an isodesmic reaction scheme leads to more effective cancellation of errors in computing enthalpies of reaction than atomization reactions or GA methods. However, as has been demonstrated by Petersson et al.,[22] the application of bond separation isodesmic reactions to the estimation of heats of formation for large molecules such as PAHs can lead to excessively large errors in the estimated value simply due to the large number of molecules involved in the isodesmic reaction. This is illustrated by reaction 1.

$$C_{10}H_8 + 12CH_4 \rightarrow 6C_2H_6 + 5C_2H_4 \qquad (1)$$

A deviation from computational error of 0.5 kcal/mol for each of these molecules could lead to a net error of 12 kcal/mol in estimating a heat of formation. Petersson et al.[22] argue that the good agreement observed by Raghavachari et al.[21] between the calculated and experimental $\Delta H_f{}^\circ{}_{298\,K}$ values for naphthalene by reaction 1 is fortuitous, and they suggested that a more appropriate reaction for naphthalene would be reaction 2.

$$C_{10}H_8 + C_2H_4 \rightarrow 2C_6H_6 \text{ (benzene)} \qquad (2)$$

The $\Delta H_f{}^\circ{}_{298\,K}$ value of benzene is known to 0.1 kcal/mol accuracy, and Petersson et al.[22] suggest that benzene should be included as a reference species for isodesmic reactions.

In evaluating the isodesmic reaction scheme, Petersson et al.[22] do not suggest a common methodology that can be applied to heavier aromatic systems. This is due to the fact that in such reaction schemes a number of isodesmic reactions can be applied to a single molecule when determining the heat of reaction (ΔH_r). For example, in the case of anthracene, several different isodesmic reactions can be generated such as using one (eq 3), two (eq 4), or three (eq 5) C_6H_6 molecules each "conserving" one, two, and three aromatic rings, respectively.

$$C_{14}H_{10} + 12CH_4 \rightarrow 6C_2H_6 + 4C_2H_4 + C_6H_6 \qquad (3)$$

$$C_{14}H_{10} + 6CH_4 \rightarrow 3C_2H_6 + C_2H_4 + 2C_6H_6 \qquad (4)$$

$$C_{14}H_{10} + 2C_2H_4 \rightarrow 3C_6H_6 \qquad (5)$$

The question would then arise as to which isodesmic reaction should be used to estimate $\Delta H_f{}^\circ{}_{298\,K}$. On the basis of the least number of molecules involved as per the argument of Petersson et al.,[22] reaction 5 would be the appropriate choice. However, it will later be demonstrated that this is not the most accurate solution and that for aromatic systems a different scheme is required compared to that used for simple hydrocarbons.

Ring Conserved Isodesmic Reactions

Bond separation isodesmic reactions conserve the bond types and numbers of each bond during the reaction and have been shown to be very reliable for estimating the thermochemical properties of hydrocarbons. However, the technique does not take into account the resonance energy in the molecule which is significant in PAHs, and thus, an isodesmic reaction scheme that preserves the aromatic nature of the PAH of interest could produce more accurate heats of formation than a BS isodesmic reaction scheme. Early group additivity schemes by Stein et al.[4] as well as in more recent work by Herndon et al.[6] showed resonance energy to be a significant contributor when calculating $\Delta H_f{}^\circ{}_{298\ K}$ for PAHs.

One method that preserves the aromatic nature of the PAH and also minimizes the number of molecules involved in an isodesmic reaction is to decompose a PAH into a number of benzene rings, which was demonstrated by Petersson et al.[22] for naphthalene, reaction 2, where two benzene rings are conserved. However, for molecules larger than naphthalene, the construction of an isodesmic reaction by simply representing each ring in any PAH molecule as a benzene ring in agreement with the suggestion of Petersson et al.[22] for naphthalene may be inaccurate (for example, reaction 5 for anthracene) because it assumes that the resonance energy is simply a multiple of the number of benzene rings a PAH can be decomposed to. Thus, a method is required that correlates properties related to aromaticity, that is, the resonance energy with the number of aromatic rings in a molecule, to allow the construction of accurate isodesmic reactions that use a smaller number of species than bond separation reactions and reflect the aromatic character of the initial species. In this work, two independent measures have been used to quantify the net aromaticity in large PAH molecules. One measure is based on the delocalization energy in these molecules, and the other is based on a delocalization index obtained from bond order alternation.

We refer to isodesmic reactions that have been constructed using the above principles of preserving aromaticity and minimizing numbers of molecules involved by decomposing PAHs to an appropriate number of benzene rings as ring conserved (RC) isodesmic reactions.

Delocalization Energy

There have been several attempts to quantify aromaticity in large PAH molecules, and a brief review is mentioned in a recent work by Matta and Hernandez-Trujillo.[23] A quantified measure of the net aromaticity of a large PAH is the key to determining the number of rings to be conserved when constructing an RC isodesmic reaction. Since aromaticity is rooted in electron delocalization, the delocalization energy appears to be the primary energetic parameter for its quantification. Wiberg[24] in a recent paper studied the structural properties and energetics for a set of linearly annelated PAHs (I−V) (the numerals after the molecular identities refer to the molecular structures of the condensed PAHs referred to in this section and the next section and can be found in Supporting Information Figure SF1) and a set of angularly annelated PAHs (VI−VIII). Using the thermochemically derived stabilization or resonance energies for benzene (I) (36 kcal/mol) and naphthalene (II) (60 kcal/mol), Wiberg[24] was able to obtain a relation for the delocalization energies in the heavier molecules based on energies obtained from DFT calculations at the B3-LYP/6-311G** level of theory. The delocalization energy (kcal/mol) as defined by Wiberg is

$$E_{\text{delocalization,M}} = 627.5[E_{\text{M}} + (-E_{\text{C}_6\text{H}_6,\text{R}}) + (n-1)(E_{\text{C}_6\text{H}_6,\text{R}} - E_{\text{C}_{10}\text{H}_8,\text{R}})] \quad (6)$$

E_M represents the calculated energy (hartrees) of the molecule of interest obtained using DFT (B3-LYP/6-31G(d) used in the present work), $E_{\text{C}_6\text{H}_6,\text{R}}$ (−231.509 849 hartrees) is the DFT energy for benzene corrected for its resonance energy (36 kcal/mol), $E_{\text{C}_{10}\text{H}_8,\text{R}}$ (−385.797 112 hartrees) is the DFT energy for naphthalene corrected for its resonance energy (60 kcal/mol), and n represents the number of rings in the molecule. The above relation was used to determine the delocalization energies (Table 1) for molecules I−VIII above using the B3-LYP/6-31G(d) level of theory which is relatively inexpensive for these large molecules. The delocalization energy per π bond (C═C) was also determined and is presented in Table 1.

TABLE 1: Delocalization Energies at B3-LYP/6-31G(d)

molecule	rings	energies (hartrees)	delocalization energy (kcal/mol)	delocalization energy/C═C (kcal/mol)
benzene	1	−231.567 219 8	36.00	12.00
naphthalene	2	−385.892 729 7	60.00	12.00
anthracene	3	−539.530 523 6	80.05	11.44
naphthacene	4	−693.165 812 5	98.54	10.95
pentacene	5	−846.799 943 6	116.30	10.57
phenanthrene	3	−539.538 656 7	85.16	12.17
chrysene	4	−693.181 939 5	108.66	12.07
picene	5	−846.826 157 6	132.74	12.07
			mean:	11.66

These delocalization energies per C═C have been used to determine the number of rings to be conserved to preserve the aromaticity of the parent molecule when constructing the isodesmic reactions. This technique automatically identifies a unique isodesmic reaction for any PAH molecule, and these reactions are referred to as the RC isodesmic reaction for that particular molecule. In agreement with Wiberg's[24] observation, the delocalization energy per C═C remains almost constant for the angularly annelated arenes, whereas, for the linearly annelated arenes, there is a small decrease as the size of the molecule increases (Table 1). The average delocalization energy based on B3-LYP/6-31G(d) calculations per C═C for this test set of eight molecules is 11.66 kcal/mol. This value can be used to determine the delocalization energy for any PAH by simply determining the number of C═C bonds in the aromatic part of the molecule. For example, in the case of naphthalene (II), it has five C═C bonds and the net delocalization energy is 58.30 kcal/mol (5 × 11.66 kcal/mol), which is close to the 60 kcal/mol value calculated from eq 6. In comparison with the delocalization energy for benzene (36 kcal/mol), the net delocalization energy for naphthalene is 1.67 times that of benzene (60/36). This implies that a reaction which conserves two benzene molecules (reaction 2) would be able to more closely represent the delocalization energy contribution to naphthalene than a scheme that conserves only one ring, and hence, a more complete cancellation of systematic errors (that accumulate because of the method and the small basis set used) is achieved. However, in the case of the larger PAH molecules, for example, anthracene (III), the Petersson et al.[22] scheme (reaction 5, decomposition of three benzene rings) does not result in complete correlation energy cancellation. Anthracene has seven C═C bonds, and hence, its net delocalization energy is 81.62 kcal/mol, which is close to the result from eq 9 of 80.05 kcal/mol. This is ∼2.22 times the delocalization energy for benzene (80.05/36), and hence, a reaction conserving two benzene rings (reaction 4) instead of three benzene rings would lead to better cancellation of errors.

The molecules in Table 1 for which the delocalization energy has been obtained belong to the class of PAH molecules referred to as cata-condensed PAHs wherein each fused carbon atom is common to no more than two rings. However, molecules such as pyrene (IX) have carbon atoms common to more than two rings and molecules of this class are referred to as peri-condensed PAHs. Equation 6 (Wiberg's relation) is valid only for cata-condensed PAHs. However, when the mean delocalization energy per C═C derived from the eight cata-condensed

TABLE 2: Aromaticity Indices Based on Electron Delocalization—Adapted from Matta and Hernandez-Trujillo[23] [a]

	aromaticity indices	
	A	B
benzene	1.000	
naphthalene	0.807	
anthracene	0.722	0.764
phenanthrene	0.863	0.650
chrysene	0.844	0.707
pyrene (IX)	0.816	0.619

[a] A refers to the two outer rings in anthracene, phenanthrene, chrysene, and pyrene, and B refers to the inner ring/rings in these molecules.

PAHs was used to estimate delocalization energies and subsequently identify the RC isodesmic reaction to be used for the peri-condensed PAHs in the test set of 30 molecules, the heats of formation were predicted with very acceptable accuracy, indicating that the mean delocalization energy per C═C bond can be used to estimate delocalization energies for a broad range of PAHs.

Aromaticity Indices

An alternative to using delocalization energies when constructing RC isodesmic reactions is to use aromaticity indices. Matta and Hernandez-Trujillo[23] have used electron delocalization indices as defined in Hartree−Fock (HF) theory as a measure of the bond order in PAHs. In agreement with Wiberg's[24] work using DFT, they obtained similar trends for one electron properties such as electron densities and ellipticity as a function of C−C bond distances using HF theory. The electron densities at the HF level of theory were used to map out the bond order in these molecules. Since the concept of aromaticity is rooted in electron delocalization, they were able to obtain aromaticity indices based on the electron density and bond order. Aromaticity indices were defined for several PAH molecules discussed in the earlier section. Table 2 gives the aromaticity indices abstracted from Matta and Hernandez-Trujillo's[23] work, and a brief discussion of the appropriate choice for RC isodesmic reaction on the basis of these indices is given below.

The aromaticity index defined for benzene is 1 which is the maximum possible for a single ring, and for all other molecules with multiple rings, the index for each ring is <1. The aromaticity index is different for the outer rings and the inner rings in molecules with multiple rings, as seen from Table 2. The net aromaticity in naphthalene is $\sim$1.61 times ($=2 \times 0.807$, Table 2) that of benzene on the basis of the derived aromaticity index. In the case of naphthalene, a RC isodesmic reaction conserving two benzene rings would be the appropriate choice. The inner ring (middle ring) in anthracene (III) is more aromatic than the two outer rings, whereas the opposite holds true for phenanthrene (VI). The net aromaticity index for anthracene is $\sim$2.21, which is obtained by summing up the individual contributions from each ring. This implies that a RC isodesmic reaction conserving two benzene rings would be a more appropriate choice (reaction 4). This result agrees with the earlier argument based on the energetics wherein the net delocalization energy in anthracene was 2.26 times that of benzene.

Matta and Hernandez-Trujillo[23] have also derived the aromaticity index in pyrene. The net aromaticity index in pyrene is 2.87 (Table 2) which indicates that three benzene rings should be conserved in the construction of a RC isodesmic reaction in agreement with the suggestion made above based on delocalization energies. The good agreement between the estimates of aromaticity based on delocalization energies and aromaticity indices for naphthalene and pyrene supports the application of delocalization energies per C═C based on the cata-condensed PAHs (Table 1) to peri-condensed PAHs such as pyrene (IX), perylene (X), and coronene (XI). Aromaticity indices derived for the two other molecules in Table 2, phenanthrene (VI) and chrysene (VII), support the net delocalization energy argument for the choice of the proper RC isodesmic reaction to be used to determine $\Delta H_f°_{298\ K}$. Phenanthrene has a net delocalization energy of 85.16 kcal/mol that is 2.37 times that of benzene and an aromaticity index of 2.38. Both measures suggest that the proper choice of RC isodesmic reaction should conserve two benzene rings. The net delocalization energy in chrysene is 3.02 (108.66/36) times that of benzene, and its net aromaticity index is 3.1. Both measures indicate that the optimum RC isodesmic reaction should conserve three benzene rings in chrysene.

Method

The focus of this work is to estimate the heats of formation for large aromatic species to an acceptable accuracy without using expensive theoretical methods to obtain energies. For the purpose of developing the technique, a set of 30 species with known experimental heats of formation which include the phenyl radical (C_6H_5) as the smallest species and diphenylanthracene ($C_{26}H_{18}$) as the largest species has been compiled.

Initially, the appropriate RC isodesmic reaction is constructed on the basis of the delocalization energy per π bond as described above. The DFT calculations are used to obtain the molecular energies and vibrational frequencies for the molecule of interest as well as the reference molecules. The energies are subsequently converted to the standard heat of formation in the gas phase ($\Delta H_f°_{298\ K}$).[12]

Results and Discussion

On the basis of calculated delocalization energies per π bond based on Wiberg's[24] scheme, a quantified measure of the aromaticity is obtained and this is applied to identify the appropriate RC isodesmic reactions (see Supporting Information Table ST1 for the list of reactions) to estimate $\Delta H_f°_{298\ K}$ for a training set of 30 aromatic and PAH molecules. The aromaticity indices derived for the smaller condensed PAHs by Matta and Hernandez-Trujillo[23] validate the delocalization energy argument with regard to the choice of the isodesmic reaction scheme. The RC isodesmic reaction scheme was tested against a wide variety of the most common aromatics and PAHs with either well-known experimental or well reviewed heats of formation. The list of molecules chosen includes small substituted single-ring aromatics such as toluene and styrene to highly substituted PAHs such as tetrahydropyrene. The set also includes the common cata- and peri-condensed PAHs (discussed in earlier sections), polyphenyls, and PAHS with five-membered rings (acenaphthylene and fluoranthene). Furthermore, the technique was applied to another 12 PAHs which have known uncertainties in their experimental measurements or for which there are no reported measurements. A compilation of the energies of 42 aromatics and PAHs at 0 K as well as their zero point energies (ZPE) at the B3-LYP/6-31G(d) level of theory is given in Supporting Information Table ST2. Also, the unscaled B3-LYP/6-31G* vibrational frequencies are given in Supporting Information Table ST3.

Table 3 shows the calculated heats of formation for the molecule set for both the RC and BS isodesmic reactions along with the number of rings conserved in the RC isodesmic

TABLE 3: $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ at B3-LYP/6-31G(d)[a]

				$\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ (kcal/mol)			absolute deviation (kcal/mol)	
no.	molecule	no. of rings	rings conserved	exptl	BS	RC	exptl-BS[b]	exptl-RC[c]
1	C_6H_5	1	1	78.00[30]	74.36	78.64	3.64	0.64
2	C_7H_7	1	1	49.44	44.61	48.91	4.83	0.53
3	C_7H_8	1	1	11.99	8.56	12.84	3.43	0.85
4	C_8H_6	1	1	97.00[31]	94.27	98.55	2.73	1.55
5	C_8H_8	1	1	35.09	31.21	35.41	3.88	0.32
6	C_8H_{10}	1	1	7.12	5.34	9.62	1.78	2.50
7	C_8H_{10}	1	1	4.28	1.61	5.90	2.67	1.62
8	C_9H_8	1	2	69.38[27]	60.64	69.21	8.74	0.17
9	C_9H_8	1	1	38.98[27]	35.54	39.82	3.44	0.84
10	$C_{10}H_8$	2	2	35.90	28.47	37.05	7.43	1.15
11	$C_{12}H_8$	2	2	100.48	90.52	99.10	8.58	1.38
12	$C_{12}H_{10}$	2	2	43.47	36.04	44.62	7.43	1.15
13	$C_{14}H_{10}$	3	2	55.13	45.23	53.79	9.90	1.34
14	$C_{14}H_{10}$	3	2	49.42	40.31	48.88	9.11	0.54
15	$C_{12}H_8$	2	2	61.62	55.69	64.27	5.93	2.65
16	$C_{16}H_{10}$	3	3	69.74	57.60	70.46	12.14	0.72
17	$C_{12}H_{10}$	2	2	37.26	32.93	41.49	4.33	4.23
18	$C_{14}H_{12}$	2	2	56.43[32]	49.22	57.80	7.21	1.37
19	$C_{11}H_{10}$	2	2	27.92	22.51	31.08	5.41	3.16
20	$C_{16}H_{10}$	4	3	53.91	50.39	56.77	3.52	2.86
21	$C_{18}H_{10}$	3	3	174.31[2]	162.4	173.21	11.91	1.10
22	$C_{18}H_{12}$	4	3	68.88[2]	55.51	68.37	13.37	0.51
23	$C_{18}H_{12}$	4	3	69.60[2]	59.80	72.66	9.80	3.06
24	$C_{18}H_{12}$	3	3	66.45[6]	54.48	67.34	11.98	0.89
25	$C_{18}H_{12}$	4	3	66.00[6]	53.77	66.63	12.24	0.63
26	$C_{18}H_{14}$	3	3	66.64[2]	54.03	66.89	12.61	0.25
27	$C_{20}H_{12}$	5	3	73.14	63.41	73.74	9.73	0.60
28	$C_{24}H_{12}$	7	4	72.18[2]	55.33	73.70	16.85	1.52
29	$C_{24}H_{18}$	4	4	91.30[2]	76.65	93.79	14.65	2.49
30	$C_{26}H_{18}$	5	4	111.28[2]	95.21	112.35	16.07	1.07
31	$\mathbf{C_{10}H_{10}}$	**1**	**1**	**34.80[5]**	**32.35**	**36.63**	**2.45**	**1.83**
32	$\mathbf{C_{12}H_9}$	**2**	**2**	**102.23[33]**	**94.26**	**102.84**	**7.97**	**0.61**
33	$\mathbf{C_{14}H_8}$	**2**	**2**	**102.77[2]**	**97.07**	**105.64**	**5.7**	**2.87**
34	$\mathbf{C_{14}H_{12}}$	**2**	**2**	**40.00[5]**	**36.16**	**44.74**	**3.84**	**4.74**
35	$\mathbf{C_{16}H_{14}}$	**2**	**2**	**38.50[5]**	**33.92**	**42.49**	**4.58**	**3.99**
36	$\mathbf{C_{18}H_{12}}$	**4**	**3**	**72.25[2]**	**63.49**	**76.35**	**8.76**	**4.10**
37	$\mathbf{C_{20}H_{10}}$	**5**	**3**	**110.83[2]**	**107.3**	**120.2**	**3.53**	**9.37**
38	$\mathbf{C_{20}H_{12}}$	**4**	**3**	**70.90[34]**	**69.57**	**82.43**	**1.31**	**11.55**
39	$\mathbf{C_{22}H_{14}}$	**5**	**4**	**81.80[2]**	**66.73**	**83.88**	**15.07**	**2.08**
40	$\mathbf{C_{22}H_{14}}$	**5**	**3**	**92.49[2]**	**82.45**	**95.30**	**10.04**	**2.81**
41	$\mathbf{C_{24}H_{12}}$	**4**	**4**	**249.9[2]**	**230.7**	**247.86**	**19.20**	**2.04**
42	$\mathbf{C_{24}H_{18}}$	**4**	**4**	**90.02[2]**	**77.19**	**94.33**	**12.83**	**4.31**
						$\mathrm{MAD_{opt}}$:[d]	8.18	1.39

[a] The experimental values were taken from NIST database unless mentioned otherwise. The molecules in bold represent molecules for which there are no experimental values or there is a possibility of an error in experimental $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ (see text). [b] exptl-BS refers to the MAD between the experimental heat of formation and the heat of formation obtained using the BS isodesmic reaction. [c] exptl-RC refers to the MAD between the experimental heat of formation and the heat of formation obtained using the RC isodesmic reaction. [d] $\mathrm{MAD_{opt}}$ refers to the mean absolute deviation for the optimum set of 30 molecules in Table 4 that excludes the molecules in bold.

reactions. The experimental heats of formation for the majority of species are taken from the NIST database.[26] The structures for the molecules listed in Table 3 are shown in Supporting Information Figure SF2. It is obvious that for molecules 1, 2, 3, 6, and 7 in Table 3 the RC isodesmic reaction that should be used should conserve only one C_6H_6 ring, since the number of π bonds is three and the net delocalization energies are approximately the same as that of benzene. Molecules 4, 5, and 9 have four π bonds, and hence, their net delocalization energies are ~47 kcal/mol which is ~1.3 times that of benzene, and hence, again, a RC isodesmic reaction conserving only one benzene ring is used to determine $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$. The only odd exception among these single-ring aromatic molecules is phenylallene which has five π bonds which suggests the use of a two benzene ring conserved reaction. The heat of formation of this molecule was taken from a recent review article by Lindstedt et al.[27] related to the thermodynamics and kinetics for the formation of aromatic species. The bond separation isodesmic reaction scheme[19] fails to reproduce the experimental $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ values accurately for even these small substituted single-ring aromatics, whereas the RC isodesmic reaction scheme is able to obtain very good agreement, with the largest error being only 2.5 kcal/mol for ethylbenzene.

Among the two-ring molecules (11, 12, 15, and 17−19, Table 3) starting with naphthalene, very good agreements with experimental values are obtained. In all these PAH molecules, a two-ring conserved isodesmic reaction was used. In the case of anthracene (13, Table 3) which forms the simplest three-ring PAH, reaction 4 was the RC isodesmic reaction that was used based on the delocalization energy arguments and it leads to a 1.34 kcal/mol absolute deviation from the experimental value, whereas the use of reaction 5 which conserves three rings leads to a 2.96 kcal/mol deviation from experiment and reaction 3 conserving one ring has a much larger deviation of 5.62 kcal/mol. The only molecules with deviations >3 kcal/mol are 1-methylnaphthalene, acenaphthene, and benzophenanthrene. A histogram depicting the deviations of calculated values from experimental values is shown for the test set of 30 molecules

TABLE 4: Comparison of $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ from Homodesmic and RC Isodesmic Reaction Schemes at the B3LYP/6-31G(d) Level of Theory

no.	molecule	$\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K,exptl}}$[a] (kcal/mol)	homodesmic absolute deviation[b] (kcal/mol)	BCGA absolute deviation[c] (kcal/mol)	RC isodesmic absolute deviation[d] (kcal/mol)
1	benzene	19.8	0.0	0.6	0.0
2	naphthalene	36.0	0.0	0.6	1.1
3	phenanthrene	48.1	0.0	0.8	0.5
4	anthracene	55.2	0.8	0.7	1.3
5	pyrene	53.9	2.1	5.9	2.9
6	triphenylene	65.5	0.1	1.3	0.9
7	benzo[*c*]phenanthrene	69.6	1.7	3.7	3.1
8	benz[*a*]anthracene	69.6	3.0	3.8	0.5
9	chrysene	63.0	1.2	0.2	0.6
10	naphthacene	79.3	1.8	3.0	4.1
11	perylene	76.4	0.1	1.9	0.6
12	coronene	73.6	1.4	4.5	1.5
13	acenaphthalene	61.7	0.0	1.3	2.7
14	fluoranthene	69.8	2.9	4.0	0.7
15	corannulene	110.2	7.3	10.3	9.4
		$\mathrm{MAD_{ref}}$:[e]	1.4	2.8	2.0
		$\mathrm{MAD_{opt}}$:[f]	1.9	3.4	2.1

[a] Experimental $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ as taken from Yu et al.[35] [b] Absolute deviation from experimental $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ using homodesmic Scheme 4 adapted from Yu et al.[35] [c] Absolute deviation from experimental $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ using the bond centered group additivity scheme adapted from Yu et al.[35] [d] Absolute deviation from experimental $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ from the RC isodesmic scheme used in the present study. Experimental values for comparison taken from Table 3. [e] $\mathrm{MAD_{ref}}$ is the mean absolute deviation for all 15 molecules including the reference molecules. [f] $\mathrm{MAD_{opt}}$ is the mean absolute deviation for molecules other than reference molecules. For the scheme of Yu et al.,[35] benzene, naphthalene, and phenanthrene are excluded. For the current RC isodesmic scheme, benzene is excluded.

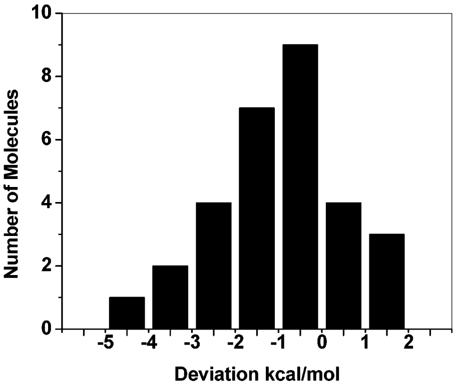

Figure 1. Histogram of errors for test set of 30 molecules. Deviation $= \Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K,exptl}} - \Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K,calcd}}$.

in Figure 1. In general, the large majority of molecules have absolute deviations <2 kcal/mol. The MAD for the training set of 30 molecules is 1.39 kcal/mol. Furthermore, within this training set, as the size of the molecule increases from single-ring aromatics to condensed PAH systems with as many as five rings, no apparent increase in absolute deviations from experimental values is observed. This offers good support for extending this scheme to obtain $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ values for larger PAH systems.

The isodesmic reaction scheme was also used to predict and evaluate $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ values for 12 PAH molecules (31−42, Table 3) which have known discrepancies in their experimental values or for which there are no experimental measurements. Dihydronaphthalene (31), dihydroanthracene (34), and tetrahydropyrene (35) all belong to the class of hydrogenated PAHs, and for these molecules, predictions using the RC isodesmic scheme were compared against group additivity estimates from the work by Shaw et al.[5] Errors >3 kcal/mol are observed for dihydroanthracene and tetrahydropyrene; however, the reported error bars for the group additivity schemes for dihydronaphthalene and tetrahydropyrene are 3 and 2 kcal/mol for dihydroanthracene, suggesting the need for an extensive review on these hydrogenated PAHs. The RC isodesmic scheme is able to reproduce $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ for *o*-biphenyl (32) and pyracylene (33) within reported error bars. Among the linearly and angularly annelated arenes, only naphthacene (36) has a calculated deviation >3 kcal/mol. However, there is a general consensus among a number of investigators[6,7,32] that the experimental $\Delta H_{\mathrm{f}}{}^{\circ}$ value for naphthacene is erroneous. The value taken for comparison here is based on a linear extrapolation derived from the linearly annelated smaller ring molecules (benzene and anthracene)[2]. The value for the five-membered linear polyacene pentacene was also taken from the same source. Corannulene (37) and benzo[*k*]fluoranthene (38) are the only molecules which show very large deviations from reported experimental values. The reported $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ value for benzo[*k*]fluoranthene is 70.9 kcal/mol which is only 1 kcal/mol larger than that of fluoranthene which has one less benzene ring. However, the current isodesmic scheme as well as an optimized homodesmic reaction scheme developed by Yu et al.[35] both predict the $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ value to be 82 kcal/mol, suggesting a review of the experimental measurement. A similar trend is observed for corannulene for which the current RC isodesmic scheme and the Yu et al.[35] homodesmic scheme both predict deviations of 9.37 and 7.3 kcal/mol, respectively, from the experimental value.

As an additional test, this newly proposed RC isodesmic scheme is compared against the optimized homodesmic reaction scheme developed by Yu et al.[35] which has been used to obtain estimates for $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ for a large number of PAHs. In this optimized scheme which forms part of a recent publication by Yu et al.,[35] a new bond centered group additivity scheme has been developed to estimate the thermochemistry of PAHs. Yu et al.[35] have evaluated the use of several reaction schemes, atomization, BS isodesmic as well as four types of homodesmic reaction schemes to estimate heats of formation using ab initio molecular energies computed at the B3LYP/6-31G(d) level of theory for a training set of 15 PAHs with well-known experimental $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ values. The primary training set of 15 molecules includes only cata- and peri-condensed PAHs, but Yu et al.[35] have also evaluated the use of their reaction schemes to predict $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ for $\mathrm{C_{60}}$ and $\mathrm{C_{70}}$ fullerenes. Yu et al.[35] concluded that a homodesmic reaction scheme (optimized scheme) with benzene, naphthalene, phenanthrene, and 1/12 $\mathrm{C_{60}}$ as reference molecules performed the best in predicting $\Delta H_{\mathrm{f}}{}^{\circ}{}_{298\ \mathrm{K}}$ for the 15 molecules as well as $\mathrm{C_{60}}$ and $\mathrm{C_{70}}$. Table 4 has been adapted from Yu et al.,[35] and a comparison against the predictions made by the RC isodesmic reaction scheme has been included for their test set. The MAD for the training set of 15 molecules is 1.4 kcal/mol with no further increase in MAD when including C_{60} and C_{70}. However, in evaluating the MAD for the training set of 15 molecules, they have also included the reference molecules benzene, naphthalene, and phenanthrene for which the errors would obviously be zero. The actual MAD for the test set of 12 molecules excluding the reference molecules is 1.9 kcal/mol using their homodesmic reaction scheme and 2.9 kcal/mol using their group additivity scheme. In comparison, the RC isodesmic reaction scheme has a MAD of 2.0 kcal/mol for the entire set of 15 molecules. The MAD is 2.1 kcal/mol when the reference molecule is excluded from the set, and this is very close to the MAD of 1.9 kcal/mol obtained by the Yu et al.[35] homodesmic scheme and is an improvement from the predictions made by their group scheme which has a MAD of 3.4 kcal/mol. Furthermore, Yu et al.[35] have restricted their reaction scheme to cata- and peri-condensed PAHs and have not tested it against substituted aromatics and PAHs. The proposed RC isodesmic reaction scheme includes only benzene as the aromatic reference molecule (which has a well characterized $\Delta H_f{}^\circ{}_{298\,K}$ value) without compromising the accuracy that is obtained by the optimized homodesmic reaction scheme proposed by Yu et al.[35] The authors are aware that the current scheme has its limitations in that it does not account for structural parameters such as ring strain and H−H repulsion which are significant contributors when considering large, floppy PAH molecules. However, considering the simplicity of the current nonparametrized method, its performance ($<$2 kcal/mol MAD) for a general test set of varied aromatics and PAHs justifies its usage and applicability to a larger set of aromatic and PAH molecules with unknown experimental $\Delta H_f{}^\circ{}_{298\,K}$ values.

Conclusions

DFT with the B3-LYP functional and the small basis set 6-31G(d) has been used to estimate $\Delta H_f{}^\circ{}_{298\,K}$ for a set of 42 aromatic and PAH molecules. Twelve of these molecules either have large uncertainties in their experimentally determined values or no measured values at all. The resonance or delocalization energy in these aromatic and PAH molecules is accounted for by the choice of a unique RC isodesmic reaction for each molecule based on an average delocalization energy per π bond. This RC isodesmic reaction scheme represents an extension of the BS isodesmic reaction scheme, with the primary difference being the inclusion of benzene as a reference molecule. The simple RC isodesmic reaction scheme represented in this study is able to do a very good job in reproducing experimental $\Delta H_f{}^\circ{}_{298\,K}$ values for the training set of 30 aromatics and PAH molecules. This test set includes molecules with well reviewed experimental measurements and with as many as six rings, with the largest molecule having 44 atoms (26 heavy atoms, C). The MAD for this test set using the RC isodesmic reaction scheme is 1.39 kcal/mol. The MAD obtained in this case is a significant improvement over that obtained using the bond separation isodesmic reaction scheme for which the MADs are ∼8 kcal/mol. The RC isodesmic scheme was also used to evaluate and predict $\Delta H_f{}^\circ{}_{298\,K}$ for 12 PAHs which have known uncertainties in their experimental measurements. The proposed RC isodesmic reaction scheme is also able to match accuracies obtained using the optimal homodesmic reaction scheme of Yu et al.[35] The small MAD when coupled with the simplicity and cost-effectiveness (computational expense) of this technique offers scope for extending this scheme to larger PAH molecules and radicals.

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Supporting Information Available: Tables showing a compilation of ring conserved isodesmic reactions for the test set of molecules used in this study (Table ST1), the absolute energies and zero point energies for the 42 molecules and the reference molecules used in this study (Table ST2), and the raw unscaled vibrational frequencies for the 42 aromatic and PAH molecules (Table ST3) and figures showing the molecular structures for condensed PAHs used to support the delocalization energy and aromaticity indices arguments (Figure SF1) and a compilation of the molecular structures of aromatics and PAHs for the test molecules in Table 3 (Figure SF2). This material is available free of charge via the Internet at http://pubs.acs.org.

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