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Converting Ab Initio Energies to Enthalpies of Formation of Free Radicals. I. New Atom Equivalents for Alkyl Radicals

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A simple method is presented to convert ab initio *computed total energies to the standard enthalpy of formation ($\Delta_f H^o$) of a large number of saturated alkyl radicals (especially those that are relatively highly branched), for which experimental data are scarcely available. For this purpose a new set of radical atom-equivalents (AEQ) and their unique combinations were defined and the energy values of the latter assigned. The theory level and the basis set requirement for the quantum chemistry calculation of the molecular energy were found to be moderate. The $\Delta_f H^o$ predictions appear to be quite accurate with reference to limited available experimental data and are better than values calculated by the group-additivity and the difference methods. The strategy provides an inexpensive way of harnessing the power of computational chemistry and combining it with the organization and insight from the group-additivity method sans any empirical corrections.* © 2011 American Institute of Chemical Engineers *AIChE J,* 58: 600–609, 2012

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Introduction

The importance of *a priori* prediction of the standard state enthalpy of formation (ideal gas, 298 K conditions, referred to in what follows as $\Delta_f H^o(298.15\ K)$ or simply $\Delta_f H^o$) of organic free radicals to both chemists and chemical engineers cannot be overstated. As transient intermediates of many industrially important classes of chemical reactions such as combustion of fossil fuels,[1] oxidation,[2] polymerizations, as well as in photochemical processes in atmospheric pollution chemistry,[3] free radicals are often the key elements of the reaction mechanism constructed to interpret complex reaction behavior. Energetics of free radicals holds great significance for the kinetics of many of the constituent elementary reactions and the discrimination among several mechanisms.

Since the early compilation of the available $\Delta_f H^o$ data for the free radicals by O'Neal and Benson,[4] several updated compilations[5–8] have appeared. A mention should be made of the CRC handbook[9] and Luo's handbook of bond dissociation energies,[10] which by and large provide useful compilation of most of the earlier published data. Despite the expanding availability of the experimental data the database for the radical enthalpy of formation, however, is still far from being comprehensive with chances of stumbling upon gaps vis-à-vis one's particular need. It should also be pointed out that not all data reported in the aforementioned compilations were obtained by direct experimental means (kinetic, spectroscopic or other methods), being sometimes derived from other measured data or from correlations. It is in this context that there is a scope for using or retooling some of the well-known empirical estimation procedures (for the

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relevant past work, prior to 2006, see Bhattacharya and Shivalkar[11]), as well as for adopting more theoretically grounded *a priori* predictive procedures.

Benson's group additivity (GA) method for estimating radical enthalpies seems to be a good general-purpose method quite suited to routine practical work giving fairly accurate results. The main handicap in more extended use of the GA method is the lack of availability of the group additivity values (GAVs) that are used in the estimation process. In our previous work[11] we had re-estimated 7 GAVs pertinent to the alkyl radicals and 22 GAVs pertinent to the oxygen-containing radicals (many of these for the first time) and the predicted $\Delta_f H^o$ values compared quite well with experimentally observed and/or other reliable published data. Recent work in our group (as yet unpublished) showed that the methodology could be extended to other radical categories.

While the above observation portends well for $\Delta_f H^o$ estimation for organic free radicals by GA method, the methodology for GAV estimation is limited being critically dependant on the availability of reliable $\Delta_f H^o$ data for the chosen set of radicals. The database for the experimental values of $\Delta_f H^o$ has many gaps and these may not be filled up in the foreseeable future. Second, although a well estimated set of GAVs themselves appear to be fairly transferable across various categories of radicals (namely, saturated, unsaturated, substituted alkyl, aromatic, oxygen, nitrogen and sulfur containing ones) for many complex structures, especially those that are heavily branched or contain rings, there has been a need for using empirical corrections to the GA estimate (many of these corrections were listed by Benson et al.[12]). There is hardly any basis (theoretical or otherwise) behind the use of such empirical corrections.

The most fundamental approach probably is to have recourse to *ab initio* computational chemistry methods for making "*a priori*" calculation of $\Delta_f H^o$, with as little dependence on the experimental data as possible.

There have been basically two main strands around which the work in this area may be grouped. In the first group one uses the best available tools for making *ab initio* total energy calculation based on an optimized geometry (additionally generating vibrational frequency, moments of inertia data), and utilizes this information to compute the atomization enthalpies of the conceptual reaction at 298 K for forming the molecule from its constituent elements. By subtracting[13] this atomization enthalpy from the experimentally determined standard enthalpies of formation of the concerned elements at 298 K, one can, in principle, calculate the standard enthalpy of formation of the molecule.

Accurate calculation of the atomization energy is a major challenge in computational chemistry that drives the increasing theory levels and the use of extended basis sets and other details involved in the energy calculations by, say, G2[14] or G3[15] theory due to Pople and his coworkers, and some of its variations and extensions[16] or the use of a particular basis set extrapolation scheme in the complete basis set (CBS)[17–18] methods due to Petersson and coworkers. Interested reader may refer to the review by van Speybroeck et al.[13] for an extended discussion on the state of art regarding the direct use of high-level quantum chemistry calculations of $\Delta_f H^o$.

All these methodologies are computationally very intensive and costly in terms of expenditure of high-grade computing power. Also despite dedicated efforts over last 2 decades it has not yet been possible to unequivocally achieve the so-called "chemical accuracy" in $\Delta_f H^o$ prediction, namely, an error of the order of $\sim$ 4 kJ/mol on the strength of computational chemistry alone. For instance, Ochterski et al.[19] had found the rms deviations of theoretical predictions by G2, G2(MP2), CBS-4 and CBS-Q model chemistries vis-à-vis experimental data for 89 molecules to be between 5.65–10.84 kJ/mol. More recently, Sayes et al.[20] had found, for a test set of 58 hydrocarbons with the carbon number ranging from 1 to 10, that even using a high-level method like CBS-QB3 the rms error was 10.21 kJ/mol in their prediction. Having recognized the known errors or possible systematic deviations in the experimental values for the enthalpy of formation of the gaseous atoms, the authors had to add empirically calculated corrections to the original experimental values (-1.29 kJ/mol per carbon atom and -0.28 kJ/mol per hydrogen atom) to bring down the rms error to levels below 4 kJ/mol.

In an impressive demonstration of the power of computational chemistry to calculate the thermochemical properties of free radicals using a sophisticated hybrid methodology named G3MP2B3, Janoscheck and Rossi[21] presented results for a varied set of free radicals that included examples from simple alkyl, unsaturated, aromatic, halogen, oxygen, nitrogen and sulfur containing radicals. The mean absolute deviation or MAD (rms value not reported) between the calculated and the experimental values of $\Delta_f H^o$ was reported to be 3.91 kJ/mol. This is probably as good as it gets, except that computationally the method is quite involved and expensive since it seeks to improve the energy calculation following a geometry optimization using B3LYP/6-31G(d), first with quadratic configuration interaction calculation and second-order Moller-Plesset perturbation theory with extended basis sets. A spin orbit correction was then included for atomic species apart from still adding what was termed "higher-level correction" to take into account the remaining deficiencies in the energy calculation.

In parallel to the aforementioned direct approach, a second strand is discernible in the literature where successful efforts have been made by a number of researchers to convert the molecular energy calculated by *ab initio*[22–30] or semiempirical methods[31] to standard gas-phase enthalpy of formation of a variety of molecular species by using certain "equivalent" ("atom" or "bond" or "group" type) with decent accuracies (in some cases close to $\sim$ 4 kJ/mol) at a fraction of the computational effort vis-à-vis the direct approach. The residual theoretical calculation errors and uncertainties in the experimental atomic enthalpy of formation data, which in any case call for empirical corrections in the aforementioned direct calculation procedures, could be shown to be subsumed as accumulated corrections as part of the atom- or group-additive equivalents. From a review of the literature on this prior art to be briefly highlighted in the next section it would appear that the demonstration of these methodologies has been predominantly concerned with organic and inorganic *molecules* except for occasional applications to a few simple radicals or ions.

In this article, a practical procedure has been devised for predicting $\Delta_f H^o$ of free radicals based on this simpler strategy wherein the power of computational chemistry that has

become routinely available to the desktop of an average engineer has been combined with the organization and insight that one inherits from the traditional GA method minus the empirical factors.

Previous work: Use of "equivalent" for a priori prediction of $\Delta_f H^o$ of molecules and radicals

The group/atom equivalent concepts—both the Wiberg's group equivalent[22] and Ibrahim and Schleyer's atom equivalent[23] approaches—were originally introduced and used in calculating $\Delta_f H^o$ based on *ab initio* self-consistent field (SCF) computations of the total energy (at a not too high-theory level and using relatively small basis sets) for molecules of several classes of organic compounds.

Wiberg[22] chose a set of group equivalents (e.g., CH_3, CH_2, CH and C groups in various structural environments), and estimated (by least squares) their energy contributions to the *ab initio* total SCF energies (at HF/6-31G(d) level) of a set of 21 hydrocarbons (acyclic, monocyclic and bicyclic alkanes and alkenes) comprising one or more of these fragments, after correcting for the pertinent experimental enthalpy of formation. Using these estimates the enthalpy of formation for a whole lot of other hydrocarbons could be calculated with a MAD vis-à-vis the experimental data of ~4–12.5 kJ/mol which is impressive considering the simplicity of the approach.

Ibrahim and Schleyer[23] extended the concept of equivalents to further detailed enumeration of atoms in different bonding environments with varying neighboring atoms. These authors used a notation of a central atom connected to various other neighboring atoms to define their atom-equivalents in the same manner as Benson et al.[12] defined the groups. However, unlike the traditional group additivity method, in this scheme, these were meant to represent an atom in a specified environment. It is these atom equivalents whose energy contributions were estimated from the *ab initio* total SCF energies (using calculations at HF/6-31G(d) level for higher accuracies although data for HF/3-21G energies were also presented) of a series of molecules after correcting for the experimental $\Delta_f H^o$ values of the pertinent molecules. Clearly, a much larger number of atom equivalents than the group equivalents were prepared and tabulated by Ibrahim and Schleyer which they used to predict the $\Delta_f H^o$ for hydrocarbons with a MAD vis-à-vis the experimental data less than 4 kJ/mol. For a host of other nitrogen and oxygen containing molecules, a few simple alkyl radicals and carbocations, fluorinated hydrocarbons, small inorganic molecules an overall MAD of about 8.4 kJ/mol was claimed. The methodology, however, fared poorly for aromatic and some strained hydrocarbons considered.

Successful results obtained, using either Wiberg or Ibrahim and Schleyer proposals, were ascribed by the authors themselves as well as others[32] to the use of basically a homodesmic reaction in which the atoms/groups of atoms constitute the reactants and the molecules the products (a sort of revised isodesmic reaction[33]). It was correctly surmised that important correlation energy corrections expected at the level of Hartree-Fock calculations used, would cancel in comparisons in this context and this allowed the use of a not too high theory level for calculation of the SCF energies. Both these approaches used total electronic energy at 0 K and did not correct for the zero point energies, for conversion from 0 to 298 K and for the presence of conformational isomers in a Boltzmann distribution. It would be fair to say that these equivalents were in effect parameterized to reproduce experimental $\Delta_f H^o$ values. To understand the basis of these assumptions it might be helpful to briefly look at the rationalization provided by many latter researchers who also extended the applications to a wide variety of molecules and used more modern versions of quantum chemistry calculations.

Although there have been many versions of the basic scheme for conversion of the molecular energy into $\Delta_f H^o$ which can be shown to reduce to the simple formulation adopted by Wiberg[22] or Ibrahim and Schleyer,[23] we have chosen to state it in a form adapted from Winget and Clark,[29] namely

$$\Delta_f H^o[i,298K] = E_{tot}[i,0K] + ZPE + (H^o[i,298K] - H^o[i,0K]) - \sum_k (H_k^o - \Delta_f H_k^o) + \sum_j a_j n[i]_j$$

where E_{tot} (i) is the sum of the electronic and the nuclear repulsion energy of the molecule i obtained from the quantum chemistry calculations. The harmonic vibrational frequencies obtained from the same calculations can be used to estimate (usually with a scaling factor) the zero-point energy *ZPE* as well as the enthalpy correction in going from 0 K to 298 K. H_k^o is the calculated enthalpy and $\Delta_f H_k^o$ is the experimental value for the enthalpy of formation of the constituent atom k in gas phase. The last term, which may be considered to provide the correction for the deficiencies in the *ab initio* energy calculation and lack of explicit corrections for anharmonicity or high-energy conformers, is constructed as an atom-additive sum, where the parameter a_j is multiplied by the number $n[i]_j$ of "atoms" (or bonds or groups) assumed to make up the molecule. The atom-additivity was intuitively presumed and was posteriori justified in terms of the repeated success in predicting $\Delta_f H^o$ by many variants of the above scheme.[24–26,29–31]

Explicitly retaining the terms associated with vibrational energy and other temperature-dependent contributions may not achieve much unless very high levels of theory are used. Also, given the significantly greater computational cost of evaluating the vibrational frequencies, these terms like other implicit deficiencies in theory may be lumped in the empirical atomic correction terms to be estimated using reliable experimental $\Delta_f H^o$ data for a small representative "training" set of molecules. If we also include the atomic enthalpy terms (considering reported uncertainties in some cases) in the same and call them as the "atom"-equivalents, we recover the scheme originally proposed by Ibrahim and Schleyer[23]

$$\Delta_f H^o[i] = E_{tot}[i] + \sum_j a_j n[i]_j$$

It is in this form that Mole et al.[27] applied the method to 23 unstrained small and stable hydrocarbons for which experimental $\Delta_f H^o$ data were well known. Density functional theory (DFT) was used for calculating molecular energies

using six different combinations of exchange and correlation functionals. However, following Dewar and O'Connor's[34] suggestion that the empirical corrections mentioned above should depend only on the atoms rather than on the bonds and groups they belong to, these authors estimated the true atom-equivalents for carbon and hydrogen from these data using the aforementioned equation (least-squares estimation). The calculated $\Delta_f H^o$ for these training set of hydrocarbons were within a rms deviation of 4.3 kJ/mol from the experimental data. The best results were obtained with Becke's three parameter hybrid DFT/HF method with Lee-Yang-Parr's correlation functional, B3LYP and 6-311G(d,p) basis set. More importantly, using the same equivalents they also predicted (in *a priori* manner) $\Delta_f H^o$ for four strained cycloalkanes, as well as benzene with a MAD of 9.6 kJ/mol, that for a set of seven simple alkyl radicals and 10 carbocations with a MAD of 7.5 kJ/mol, which are less than or comparable with those obtained by Ibrahim and Schleyer[23] with a much larger number of atom equivalents.

Guthrie[28] on the other hand considered atom equivalents for molecules involving carbon, hydrogen, oxygen, nitrogen, sulfur and phosphorus along the line taken by Ibrahim and Schleyer[23] using different parameters for each coordination number, with an additional parameter for carbon in an aromatic ring and making no distinction between the pyramidal and plannar geometry for the tricoordinate nitrogen. Using DFT calculations for the total energy of the molecules [B3LYP/6-31G(d,p)//rhf/6-31G(d,p),] the $\Delta_f H^o$ data for 250 molecules that use 18 such atom equivalents could be fitted (least squares) with a standard deviation of 12.4 kJ/mol. The author generalized the above treatment and devised two more types of equivalents, namely, the bond and the group equivalents whose contributions can be accumulated in much the same manner as for the atom equivalents and provided least squares estimates for the same. Using 40 bond equivalents $\Delta_f H^o$ data for 229 molecules could be fitted to within a standard deviation of 7.95 kJ/mol, and for the group contribution scheme (using Benson et al.'s[12] group definitions with a slightly modified notation) 79 equivalents were needed to fit the $\Delta_f H^o$ data for 183 molecules with a standard deviation of 5.8 kJ/mol only.

Winget and Clark[29] extended the application of atom-equivalent methodology to 845 molecules containing elements H, C, N, O, F, Al, Si, P, S, and Cl using hybrid density functional theory (single-point energy calculations on the B3LYP/6-31+G(*d*) optimized geometries were performed using the 6-311+G(3*df*,2*p*) basis set), and provided evidence to the robustness and a realistic estimate of overall accuracy of the atom-additive schemes for predicting enthalpies of formation of a large number and variety of molecules at 298 K.

Repasky et al.[31] used the scheme popularized by Allinger et al.[24], 61 bond and group equivalents of the same lineage and computationally less demanding semiempirical methods for energy computation. For a set of 583 neutral, closed-shell molecules containing carbon, hydrogen, nitrogen and oxygen the MAD was found to be 9.6, 9.2 and 12.5 kJ/mol for the AM1, PM3 and MNDO methods, respectively.

Ibrahim and Schleyer[23] had considered free radicals in a rudimentary way by introducing a carbon centered radical atom and $\Delta_f H^o$s were calculated for only eight simple free radicals with an average absolute deviation of more than 6.3 kJ/mol. Mole et al.[27] considered the same set of radicals and claimed to obtain similar results using just one carbon parameter for both alkanes and the alkyl radicals To our knowledge, there does not seem to be any attempt in published literature on a systematic adaptation of either the group or the atom-equivalent methodology to predict the enthalpy of formation of free radicals.

Table 1. List of Alkane Atom Equivalents

Atom Equivalents	Symbol
H-C	A
$C\text{-}(C)(H)_3$	P
$C\text{-}(C)_2(H)_2$	S
$C\text{-}(C)_3(H)$	T
$C\text{-}(C)_4$	Q

Distinguishing features of the new work

In this work, we have extended the atom equivalent scheme with regard to saturated alkyl radicals as a first step in our goal to establish accurate yet simple and practical methodologies based on first principles for *a priori* prediction of standard enthalpy of formation of free radicals. This choice was motivated by the availability of reliable experimental $\Delta_f H^o$ data at least for a few simple small alkyl radicals (which could be used for the parameterization and testing), and the fact that for a much larger range of longer chain alkyl radicals with/without branching, experimental data are generally not available. Accurate *a priori* predictions would be desirable for both theoretical studies and practical applications such as studies in oxidation and combustion or atmospheric pollution chemistry.[35]

The major distinction with the previous work is that we have considered seven different atoms (in Benson et al.'s nomenclature) comprising three radical centered and four radical adjacent carbon atoms to represent all possible combinations for building up any alkyl radical. Second, based on the computed SCF energies and the experimental $\Delta_f H^o$ data for a chosen set of alkanes and alkyl radicals, it has been possible to assign unique values to the desired molecular atom equivalents, and a set of binary and ternary combinations of the radical atom equivalents (instead of individual equivalents). This scheme has then allowed us to predict $\Delta_f H^o$ of all the other alkyl radicals, *not used in the parameter estimation*. The new method does not use any empirical structural corrections unlike the GA method and provides results as accurate or better. In what follows we describe the method in detail.

The alkane and the alkyl radical atom equivalents

Following Ibrahim and Schleyer[23] we define five atoms (hence, we term these as "atom equivalents"), which can be used to build any alkane molecule. These are listed in Table 1 with the appropriate symbols assigned to primary, secondary, tertiary and quaternary carbon atoms and to the hydrogen atom connected to any of these carbon atoms. In Table 2 are listed five chosen alkane molecules BA_1 to BA_5 (first three are the simplest ones and the other two with moderate

Table 2. Aggregate Atom Equivalent (AEQ) Energies for the Basis Alkanes

Alkane	Structure	AEQs [frequency]	Aggregate AEQ energy
Methane (BA_1)	CH_4	H-C [4], C-(C)$(H)_3$ [1]	$4E_A+E_P$
Ethane (BA_2)	CH_3CH_3	H-C [6], C-(C)$(H)_3$ [2]	$6E_A+2E_P$
Propane (BA_3)	$CH_3CH_2CH_3$	H-C [8], C-(C)$(H)_3$ [2], C-$(C)_2(H)_2$ [1]	$8E_A+2E_P+E_S$
2-methyl propane (BA_4)	$CH_3CH(CH_3)CH_3$	H-C [10], C-(C)$(H)_3$ [3], C-$(C)_3$(H) [1]	$10E_A+3E_P+E_T$
3,3-dimethyl butane (BA_5)	$CH_3C(CH_3)_2CH_2CH_3$	H-C [14], C-(C)$(H)_3$ [4], C-$(C)_2(H)_2$ [1], C-$(C)_4$ [1]	$14E_A+4E_P+E_S+E_Q$

branching, together, henceforth, termed "basis alkanes") along with the constituent atom equivalents from Table 1, with their frequency of occurrence in a given molecule. In the final column of this table appears the aggregate energy of these atom equivalents for each molecule. Table 3 summarizes five linear equations that can be used to calculate the desired atom equivalent energy contributions, using the experimental $\Delta_f H^o$ data for these basis alkanes and their computed total SCF energies.

Having demonstrated the basic calculation procedure, we now list in Table 4 seven alkyl radical atom equivalents (along with the symbols), and summarize in Table 5 the aggregate energy of these radical atom equivalents corresponding to seven chosen ("basis") alkyl radicals in the same way as it was done in Table 2 for the alkanes. While it should be possible, in principle, to calculate energy contribution values for all the seven alkyl radical atom equivalents, we have chosen to parameterize these rather as combinations of the equivalents. This was prompted by an insight gained from our earlier work on $\Delta_f H^o$ prediction for free radicals by using the GA method.[11] A little reflection tells us that all the alkyl radicals considered here comprise of at least one radical centered and one radical adjacent carbon atoms. For instance, an isopropyl radical can be seen to be constituted from a combination of one $C^{\bullet}$-$(C)_2(H)$ and two C-$(C^{\bullet})(H)_3$ radical atom equivalents. Thus in the last column of Table 5, one can easily identify seven (six binary and one ternary) combinations of radical equivalents, energy contributions for which can be uniquely evaluated using the computed SCF energy and the experimental data on $\Delta_f H^o$ for the seven basis radicals (apart from the values for the two alkane atom equivalents already determined as above). Thus, once the total SCF energy of the five molecular and the seven radical species were obtained by using a quantum chemical method (using a standard code) it is a simple matter to setup the aforementioned calculations in an Excel spreadsheet and get the desired quantities quickly and conveniently.

Once these 12 parameters were evaluated, the *ab initio* energy of each of the other (nonbasis) alkyl radicals was used to calculate in a routine manner the corresponding enthalpy of formation value using the same spreadsheet. It will be shown later in the article that any other combination of the radical atom equivalents (that may arise with reference to any alkyl radical) may be reduced to some combinations of these seven unique combinations.

Table 3. Equations for Evaluating the Alkane AEQ Energies

$4A + P \Leftrightarrow BA_1$	$\Delta_f H^o_{BA_1} = E_{BA_1} - 4E_A - E_P$
$6A + 2P \Leftrightarrow BA_2$	$\Delta_f H^o_{BA_2} = E_{BA_2} - 6E_A - 2E_P$
$8A + 2P + S \Leftrightarrow BA_3$	$\Delta_f H^o_{BA_3} = E_{BA_3} - 8E_A - 2E_P - E_S$
$10A + 3P + T \Leftrightarrow BA_4$	$\Delta_f H^o_{BA_4} = E_{BA_4} - 10E_A - 3E_P - E_T$
$14A + 4P + S + Q \Leftrightarrow BA_5$	$\Delta_f H^o_{BA_5} = E_{BA_5} - 14E_A - 4E_P - E_S - E_Q$

Computation of molecular energies

In this work, the *ab initio* SCF energies of the molecules and the radicals were computed using two different methodologies (implemented with two different commercially available software). In the first, we used Hartree-Fock theory with 6-31G(d) basis set with appropriate spin assignment for the radicals (UHF), and the molecules (RHF), and assuming neutral species. This basis set was shown by earlier workers[22–23] to be optimum in terms of calculation effort and accuracy of the final results. The energy calculations were preceded by the geometry optimization at the same basis set level. These calculations were done using Gaussian 03[36] for Windows software (Gaussian, Inc., USA) installed on a HP xw6600 workstation with Windows XP operating system. The molecular structures were conveniently input to the Gaussian using GaussView (vs 4.1) software (Gaussian, Inc., USA). We also setup/drew the molecules and the radicals using another freely available software (wxMacMolPlt[37]) and the molecular structural information in Gaussian compatible format were generated and transferred to the Gaussian input files with identical results.

In the second method, we used DFT calculations implemented in the DMOL software code[38–39] as a part of the Material Studio software (vs 4.20) suite from Accelrys, Inc., USA, with its own visualizer code for drawing the molecules and the radicals, and generating the structural input data to be used by DMOL. The DFT calculations were done with unrestricted spin for the radicals (and restricted one for the molecules), Becke's exchange functional with Lee-Yang-Parr's correlation functional (BLYP) and DNP basis set (double numeric quality basis set with polarization functions, said to be comparable in size with HF/6-31G(d,p) basis set although providing more accurate results). This suite installed on a HP make cluster computer system (dual core dual CPU 32 node Intel Xeon processor, a central facility at National Chemical Laboratory, Pune, India) was accessed on the remote server with the jobs run on the cluster and result files retrieved locally.

Table 4. List of Alkyl Radical Atom Equivalents

Atom Equivalents	Symbol
$C^{\bullet}$-$(C)(H)_2$	a
$C^{\bullet}$-$(C)_2(H)$	b
$C^{\bullet}$-$(C)_3$	c
C-$(C^{\bullet})(H)_3$	d
C-$(C^{\bullet})(C)(H)_2$	e
C-$(C^{\bullet})(C)_2(H)$	f
C-$(C^{\bullet})(C)_3$	g

Table 5. Aggregate Atom Equivalent (AEQ) Energies for the Basis Alkyl Radicals

Alkyl radical	Structure	AEQs [frequency]	Aggregate AEQ energy
Ethyl	$CH_3CH_2^{\bullet}$	H-C [5], $C^{\bullet}$-(C)$(H)_2$ [1], C-($C^{\bullet}$)$(H)_3$ [1]	$5E_A+E_a+E_d$
1-propyl	$CH_3CH_2CH_2^{\bullet}$	H-C [7], C-(C)$(H)_3$ [1], $C^{\bullet}$-(C)$(H)_2$ [1], C-($C^{\bullet}$)(C)$(H)_2$	$7E_A+E_P+E_a+E_e$
Isopropyl	$CH_3CH^{\bullet}CH_3$	H-C [7], $C^{\bullet}$-$(C)_2$(H), C-($C^{\bullet}$)$(H)_3$ [2]	$7E_A+ E_b+2E_d$
t-butyl	$CH_3C^{\bullet}(CH_3)$ CH_3	H-C [9], $C^{\bullet}$-$(C)_3$ [1], C-($C^{\bullet}$)$(H)_3$ [3]	$9E_A+ E_c+3E_d$
2-methyl 1-propyl	$CH_3CH(CH_3)CH_2^{\bullet}$	H-C [9], C-(C)$(H)_3$ [2], $C^{\bullet}$-(C)$(H)_2$ [1], C-($C^{\bullet}$)$(C)_2$(H)	$9E_A+2E_P+ E_a+E_f$
2,2-dimethyl 1-propyl	$CH_3C(CH3)_2CH_2^{\bullet}$	H-C [11], C-(C)$(H)_3$ [3], $C^{\bullet}$-(C)$(H)_2$ [1], C-($C^{\bullet}$)$(C)_3$	$11E_A+3E_P+ E_a+E_g$
2-methyl 2-butyl	$CH_3C^{\bullet}(CH_3)CH_2CH_3$	H-C [11], C-(C)$(H)_3$ [1], $C^{\bullet}$-$(C)_3$ [1], C-($C^{\bullet}$)$(H)_3$ [2], C-($C^{\bullet}$)(C)$(H)_2$	$11E_A+E_P+ E_c+2E_d+ E_e$

It was clear from the previous work that the recent trend has been toward using DFT calculations. The purpose of using two distinctly different methods in this study is to be able to examine if numerically different energy values (and, hence, different set of values for the atom equivalent contributions) would make any impact on the prediction of $\Delta_f H^o$ values.

Results and Discussion

Atom equivalent energy values

For convenience of presentation, the results on parameterization of the atom equivalents are grouped according to the method of energy calculations, namely, the molecular orbital (MO) method and the density functional approach (DFT) as mentioned above and presented in parallel in the tables.

Table 6 presents the computed total energies at 0 K (by both methods) for the basis alkanes and Table 7 the energies for the basis radicals in the usual atomic units, hartrees or Ha. All *ab initio* energies [$E^o(0)$] refer to a single conformation of a given molecule or a radical in the vibrationless state. Zero point energy corrections or conversion from 0 to 298 K were not included. Early trials with these corrections to energy values did not show much improvement in the prediction of $\Delta_f H^o$ while raising the computational effort significantly for doing the frequency calculations. Both the tables also summarize the corresponding experimental standard enthalpy of formation data from the published literature. A note of caution should be added about the experimental data. For some of the primary alkyl radicals the literature reports a number of experimental observations by many researchers over past several decades leading to a bit of controversy about the accuracy of some of these data. Our selection was guided, generally, by data that are of more recent origin and those that reported less standard deviations than others, although there may have been exceptions due to paucity of availability of data.

Table 6. Total Electronic Energies (at 0 K) and the Enthalpy of Formation for the Basis Alkanes

	$E^o(0)$/Ha		
Alkane	UHF/6-31G(d)	BLYP/DNP	$\Delta_f H^o$/kJ mol^{-1}
methane (BA_1)	−40.19517192	−40.5017501	−74.48[40]
ethane (BA_2)	−79.22875496	−79.8023673	−83.85[40]
propane (BA_3)	−118.26365102	−119.1048116	−104.68[40]
2-methyl propane (BA_4)	−157.2989779	−158.4075123	−134.18[40]
2,2-dimethyl butane (BA_5)	−235.36460501	−237.0087277	−185.56[41]

Using the aggregate energies of basis alkane atom equivalents as set out in Table 2 and the equations in Table 3, the energy contributions for these equivalents were evaluated and are presented in Table 8. The tabulated electronic energies per molecule/radical were converted to per mole by multiplying with a conversion factor 2625.4996 kJ/mol. Similarly, using the expressions for the specified combinations of the basis radical equivalents (Table 5), energy values for the alkane equivalents (Table 8) and the $\Delta_f H^o$ values from Table 7, the energy contributions for the combinations of radical atom-equivalents were evaluated and are set out in Table 9. As expected, the atom equivalent energy values in Tables 8 and 9 are marginally different just like the precursor energies of the molecules and the radicals calculated by the two different methods.

Validation of the AEQ based prediction

Having identified the key atom equivalents or their combinations and determined their energy values it remains to be shown how predictions of $\Delta_f H^o$ made using these for a few longer chain and/or branched alkyl radicals (not used as the basis radicals) compare them with the published experimental (wherever available), and/or calculated (e.g., estimated using bond energy values) $\Delta_f H^o$ values. This comparison has been presented in Table 10 for AEQs estimated from MO calculations and Table 11 shows similar comparison for the AEQs estimated using DFT. Apparently the energy calculation method does not seem to cause much of a difference in the predicted $\Delta_f H^o$ values. The average absolute deviation for this set of six radicals was found to be 2.29 kJ/mol, and a standard deviation of 2.69 kJ/mol using MO calculations. The corresponding numbers with DFT calculations are 2.35 and 2.76 kJ/mol, respectively. As mentioned earlier, the atom equivalent combination b + d + e required to

Table 7. Total Electronic Energies (at 0 K) and the Enthalpy of Formation for the Basis Alkyl Radicals

	$E^o(0)$/Ha		
Alkyl radical	UHF/6-31G(d)	BLYP/DNP	$\Delta_f H^o$/kJ mol^{-1}
Ethyl	−78.59714864	−79.1363409	118.83[42]
1-propyl	−117.63143369	−118.4379554	99.998[6]
isopropyl	−117.63613637	−118.4453604	87.864[43]
t-butyl	−156.67500854	−157.753866	51.46[44]
2-methyl 1-propyl	−156.66647817	−157.7405598	66.11[45]
2,2-dimethyl 1-propyl	−195.7010414	−197.0424305	36.4[5]
2-methyl 2-butyl	−195.70744956	−197.0539327	29.29[46]

Table 8. AEQ Energy Values for the Basis Alkanes

AEQ Energy	Value/Ha	
	MO	DFT
E_A	−0.568396034	−0.588168044
E_P	−37.89322125	−38.12071139
E_S	−37.89016774	−38.11817196
E_T	−37.88424624	−38.11259012
E_Q	−37.8733305	−38.10268027

represent branched alkyl radicals such as 2-butyl could be resolved in terms of the equivalent combination of already parameterized combinations a + d, a + e and b + 2d.

Comparison of AEQ based prediction with other common methods

For a lot many other alkyl radicals, larger ones or especially those with significant branching, no experimental data are available. Prediction is the only recourse one has. Cohen[35] had identified about 24 such alkyl radicals and devised what was called a ''Difference method'' to estimate $\Delta_f H^o$ of the radicals from the known (or estimated) $\Delta_f H^o$ value of the parent hydrocarbons, and a value for the energy of dissociation of a C-H bond (different values were set for a primary, secondary or a tertiary carbon atom).

In an earlier article from our group[11] we had predicted $\Delta_f H^o$ for these latter group of radicals by the group additivity (GA) method using a set of group additivity values (GAV) for the seven pertinent radical groups (three so-called ''radical centered groups'' and four ''radical adjacent groups''), which were evaluated therein by a new methodology. In a recent modification and extension of this methodology to a much larger range of free radicals (to be published separately), we had re-evaluated the values of all the alkyl radical GAVs (which are, therefore, slightly different from those reported in Table 3 of our earlier article[11]), and redid the predictions following the GA procedure[11] for all these radicals. These results appear along with the estimates reported by Cohen[35] in the fourth and the fifth columns of Table 13, respectively. The estimates are compared with the AEQ based $\Delta_f H^o$ predictions (appearing in the second and third columns of the same table corresponding to SCF energies calculated by the MO and the DFT methods, respectively, the latter having been summarized in Table 12). With reference to the difference method, the GA method shows an average absolute deviation of 2.78 and a standard deviation of 3.79 kJ/mol, while the AEQ method using MO based energy calculations shows 2.17 and 2.98 kJ/mol for the same quantities. The AEQ based method using DFT based energy calculations shows an even better average absolute deviation of 1.71 and a standard deviation of 2.41 kJ/mol. Clearly the AEQ method seems more accurate and shows less deviations than the GA method which, however, shows acceptable accuracy. However, the AEQ method does not have to use any empirical structural corrections.

Table 9. AEQ Combination Energy Values for the Basis Alkyl Radicals

AEQ Combination Energy	Value/Ha	
	MO	DFT
E_a+E_d	−75.80042744	−76.24075965
E_a+E_e	−75.79752785	−76.23815535
E_b+2E_d	−113.6908303	−114.3616502
E_c+3E_d	−151.5790458	−152.4799552
E_a+E_f	−75.78965065	−76.23080391
E_a+E_g	−75.78288582	−76.22431239
$E_c+2E_d+E_e$	−151.5730273	−152.4645282

A priori prediction of $\Delta_f H^o$ for cycloalkanes

So far all the examples belonged to straight chain alkyl radicals. Although atom equivalents were evaluated using mostly simple straight chain alkyl basis radicals, these were found to be effective in predicting the $\Delta_f H^o$ for a large number of longer and/or branched alkyl radicals, without any need to add empirical structural corrections. Now we turn our attention to a selection of typical cycloalkyl radicals for whom the GA method requires to use corrections[11] for each type of ring (like Benson et al.[12] used in the cases of cycloalkanes). In this work, we went ahead and applied the atom equivalent methodology to the cycloalkyl radicals for making truly *a priori* prediction of the $\Delta_f H^o$ in the same way as before. In constituting the aggregate energy of the atom equivalents for cyclopropyl through cycloheptyl radicals, we required the contribution $E_b + 2E_e$ apart from the contribution for the secondary alkane atom equivalent, E_S (tabulated in Table 8). The $E_b + 2E_e$ contribution is found by combining the contributions $E_a + E_d$, $E_a + E_e$ and $E_b + 2E_d$ (obtained from Table 9). For the spiropentyl radical we needed the contribution $E_b + E_e + E_g$, which was found by combining $E_a + E_d$, $E_a + E_e$, $E_a + E_g$ and $E_b + 2E_d$. The results have been presented in Tables 14 using DFT based energy calculation only as it gave slightly better results. No corrections or adjustments were used in these calculations. When compared with previously published experimental

Table 10. Comparison of AEQ Based Predictions (Energy by MO Calculations) of Radical Enthalpy of Formation with the Published Experimental/Estimated Data

Radical	Structure	Aggregate AEQ energy/Ha	$E^o(0)$/Ha [UHF/6-31G(d)]	$\Delta_f H^o$/kJ mol^{-1}	
				AEQ	Reported
1-butyl	$CH_3CH_2CH_2CH_2^\bullet$	$9E_A+E_P+E_s+(E_a+E_e)$	−156.6665603	78.56	77.82[47]
2-butyl	$CH_3CH_2C^\bullet HCH_3$	$9E_A+E_P+(E_b+E_d+E_e)$*	−156.670678	68.36	67.78[48]
1-pentyl	$CH_3CH_2CH_2CH_2CH_2^\bullet$	$11E_A+E_P+2E_s+(E_a+E_e)$	−195.7012461	58.27	54.39[49]
2-pentyl	$CH_3CH_2CH_2C^\bullet HCH_3$	$11E_A+E_P+E_s+(E_b+E_d+E_e)$*	−195.7054626	47.82	50.21[49]
1-hexyl	$CH_3CH_2CH_2CH_2CH_2CH_2^\bullet$	$13E_A+E_P+3E_s+(E_a+E_e)$	−234.7357607	38.44	33.47[49]
2-hexyl	CH_3CH_2 $CH_2CH_2C^\bullet HCH_3$	$13E_A+E_P+2E_s+(E_b+E_d+E_e)$*	−234.7401519	27.53	29.29[49]

*$(E_b+E_d+E_e) = (E_a+E_e)+(E_b+2E_d)-(E_a+E_d)$

Table 11. Comparison of AEQ Based Predictions (Energy by DFT Calculations) of Radical Enthalpy of Formation with the Published Experimental/Estimated Data

Radical	Structure	Aggregate AEQ energy/Ha	$E^o(0)$/Ha (BLYP/DNP)	$\Delta_f H^o$/kJ mol^{-1} AEQ	$\Delta_f H^o$/kJ mol^{-1} Reported
1-butyl	$CH_3CH_2CH_2CH_2^{\bullet}$	$9E_A+E_P+E_s+(E_a+E_e)$	−157.7404302	79.08	77.82[47]
2-butyl	$CH_3CH_2C^{\bullet}HCH_3$	$9E_A+E_P+(E_b+E_d+E_e)$*	−157.7472738	68.25	67.78[48]
1-pentyl	$CH_3CH_2CH_2CH_2CH_2^{\bullet}$	$11E_A+E_P+2E_s+(E_a+E_e)$	−197.0426546	58.82	54.39[49]
2-pentyl	$CH_3CH_2CH_2C^{\bullet}HCH_3$	$11E_A+E_P+E_s+(E_b+E_d+E_e)$*	−197.0495644	47.82	50.21[49]
1-hexyl	$CH_3CH_2CH_2CH_2CH_2CH_2^{\bullet}$	$13E_A+E_P+3E_s+(E_a+E_e)$	−236.344889	38.54	33.47[49]
2-hexyl	CH_3CH_2 $CH_2CH_2C^{\bullet}HCH_3$	$13E_A+E_P+2E_s+(E_b+E_d+E_e)$*	−236.3516697	27.87	29.29[49]

*$(E_b+E_d+E_e) = (E_a+E_e)+(E_b+2E_d)-(E_a+E_d)$

(wherever available) and/or estimated predictions for the cyclobutyl, cyclopentyl and the cyclohexyl the results were almost as accurate as was obtained for other radicals in this article. It is to be noted that for a strained structure such as spiropentyl radical the AEQ based predictions were reasonably close although not as good as for some other radicals.

Concluding Remarks

This article is concerned with the adaptation and extension of the atom equivalent (AEQ) method in order to make *a priori* prediction of the $\Delta_f H^o$ of a large number of saturated alkyl radicals (especially those that are relatively highly branched) for which experimental data are scarcely available. The predictions appear to be quite accurate with reference to limited available experimental data (with a precision of about 2.4 kJ/mol), and are also better than values calculated by the our own adaptation of the GA method[11] or those by the so-called difference method by Cohen.[35]

The AEQ method, unlike the traditional GA method, does not require the use of any empirical structural corrections. The required atom equivalent contributions were determined by using published $\Delta_f H^o$ data for a limited number of simple alkanes and alkyl radicals. The theory level and the basis set requirement for the *ab initio* quantum chemistry calculation of the molecular energy were shown to be quite moderate. The choice of energy calculation method (MO or DFT based) did not show significant influence on the accuracy or the precision of the results at least for the class of free radicals considered.

With the easy availability of the commercial software implementing these calculations, predicting $\Delta_f H^o$ for many classes of radicals should be well within the reach of chemical engineers. It was shown, for example, straightforward attempt to predict $\Delta_f H^o$ for cycloalkyl radicals met with reasonable success. However, more work will be required involving definition of other atom equivalents or their combinations (and the evaluation of the energy contributions) in respect of other classes of organic free radicals and resolving issues related to transferability of parameters, if any, across various radical types. Once such a complete set of parameters are available the AEQ method is likely to become the

Table 12. Total SCF Energy of the Alkyl Radicals by MO and DFT Methods

Radical	$E^o(0)$/Ha (MO)/Ha	$E^o(0)$/Ha (DFT)/Ha
1-butyl	−156.6665603	−157.7404302
2-butyl	−156.670678	−157.7472738
1-pentyl	−195.7012461	−197.0426546
2-pentyl	−195.7054626	−197.0495644
1-hexyl	−234.7357607	−236.344889
2-hexyl	−234.7401519	−236.3516697
1-ethyl propyl	−195.704598	−197.0492866
2-methyl butyl	−195.6993523	−197.0412777
1,2-dimethyl propyl	−195.7049538	−197.0471023
3-methyl butyl	−195.7010301	−197.0427914
1-ethyl butyl	−234.7399653	−236.3514733
2-methyl pentyl	−234.7342317	−236.3432823
1,1-dimethyl butyl	−234.7431723	−236.357191
1,3-dimethyl butyl	−234.739898	−236.3510214
4-methyl pentyl	−234.7344064	−236.3438948
3-methyl pentyl	−234.7325368	−236.3433957
1,2-dimethyl butyl	−234.7388685	−236.3487027
1-methyl 1-ethyl propyl	−234.7409561	−236.3539108
2-ethyl butyl	−234.732154	−236.3435182
2,3-dimethyl butyl	−234.731979	−236.3421212
1,1,2-trimethyl propyl	−234.7385248	−236.3543949
2,2-dimethyl butyl	−234.7318714	−236.3415107
1,2,2-trimethyl propyl	−234.7374298	−236.3490392
3,3-dimethyl butyl	−234.7343932	−236.3442364

Table 13. Comparison of AEQ Based Predictions of Alkyl Radical Enthalpy of Formation with the GA and the Difference Methods

Radical	$\Delta_f H^o$/kJ mol^{-1} AEQ (MO)	AEQ (DFT)	GA	Difference[35]
1-butyl	78.56	79.08	74.06	76.90
2-butyl	68.36	68.25	63.81	66.86
1-pentyl	58.27	58.82	53.14	55.61
2-pentyl	47.82	47.82	42.89	45.56
1-hexyl	38.44	38.54	32.22	35.40
2-hexyl	27.53	27.87	21.97	25.36
1-ethyl propyl	50.49	48.38	38.33	45.56
2-methyl butyl	50.58	49.80	48.53	48.79
1,2-dimethyl propyl	36.49	41.65	38.28	38.74
3-methyl butyl	51.31	50.48	46.44	48.79
1-ethyl butyl	28.42	28.22	17.41	25.36
2-methyl pentyl	29.79	30.12	27.61	27.70
1,1-dimethyl butyl	6.28	6.31	10.79	5.52
1,3-dimethyl butyl	20.66	21.59	15.27	17.66
4-methyl pentyl	34.46	33.16	25.52	27.70
3-methyl pentyl	39.37	34.47	28.87	30.42
1,2-dimethyl butyl	18.23	23.03	20.71	20.46
1-methyl 1-ethyl propyl	12.50	14.76	9.58	8.24
2-ethyl butyl	35.24	29.50	30.96	30.42
2,3-dimethyl butyl	28.17	25.18	20.92	24.23
1,1,2-trimethyl propyl	5.82	1.02	2.85	2.05
2,2-dimethyl butyl	26.24	24.40	24.69	16.40
1,2,2-trimethyl propyl	12.26	11.77	14.43	6.36
3,3-dimethyl butyl	13.86	12.91	14.23	16.40

Table 14. Comparison of AEQ Based Predictions (Energy by DFT Calculations) of Cycloalkyl Radical Enthalpy of Formation with GA Method and Published Experimental/Estimated Data

		$\Delta_f H^o$/kJ mol^{-1}		
Radical	$E^o(0)$/Ha	AEQ	GA	Reported
Cyclobutyl	−156.5092147	216.80	213.22	214.22[5]
Spiropentyl	−194.5579153	362.85	380.45	380.74[5]
Cyclopentyl	−195.8417703	116.91	109.87	107.11[50]
Cyclohexyl	−235.1521505	75.23	62.17	75.31[51]
Cycloheptyl	−274.4493702	68.11	66.78	51.04[5]

preferred one for prediction of $\Delta_f H^o$ of free radicals in the absence of reliable experimental data.

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