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Reviews

Re-tooling Benson's Group Additivity Method for Estimation of the Enthalpy of Formation of Free Radicals: C/H and C/H/O Groups

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Enthalpy of formation of free radicals is often required for the discrimination of reaction mechanisms (for complex processes such as combustion, hydrocarbon oxidation, or decomposition of peroxides and hydroperoxides) involving both molecular species and free radicals. Despite the expanding availability of the experimental measurements, the database for the enthalpy of formation of radicals is still not comprehensive. One of the simplest, efficient, and reliable methods for estimating the quantity for organic radicals from their molecular structure is the group-additivity method due to Benson and co-workers. Perusal of the literature shows that the group-additivity values (GAV) for many radical groups have remained either undetermined or obtained by assignment to the corresponding molecular groups without justification. In this paper, we devise simple methodologies to evaluate GAVs for a number of new oxygen-containing radical groups and re-estimate several alkyl and oxygen-containing radical groups using experimental data on the radical enthalpy of formation. The validity of these GAVs has been established by comparing the predicted enthalpies with experimental data. Finally, some of these updated GAVs were used in estimating the enthalpy change associated with the typical elementary steps in a peroxide decomposition reaction.

Introduction

Simple, efficient, and reliable methods for estimation of properties of organic compounds from their molecular structure are always in demand in the design of products and processes. In modern computer-aided calculations involved in process design and simulation reliable and accurate property estimation methods play an important role. Enthalpy of formation of various species (simple molecules or complexes, ions, radicals) is one such important thermodynamic data. A great many chemical processing operations involve one or more chemical reaction steps such as

$$A + B \Leftrightarrow C + D \tag{1}$$

Associated enthalpy of reaction ($\Delta_r H$) determines the provision to remove or supply heat so as to maintain the desired reaction temperature. Enthalpy of reaction, in turn, can be calculated knowing the enthalpy of formation of the various reactant and the product species participating in the reaction.

In the context of understanding the nature of complex chemical processes such as oxidation and combustion or the atmospheric pollution chemistry, detailed kinetic models[1,2] have been constructed. These models are comprised of elementary reactions involving both molecular and radical species. Though not of comparable richness of details and complexity, for commercially important liquid-phase oxidation processes such as cyclohexane oxidation, free radical-based reaction networks are being considered[3,4] for modeling purposes in preference to mere empirical rate laws. The availability of thermochemical data has come to acquire critical value to both chemists and chemical engineers. Especially for discrimination among reaction mechanisms involving free radicals and other reactive intermediates, the data pertaining to enthalpy of formation, not just of usual organic molecules but also that of a number of radicals, are important.

Several sources[5,6] exist for the data on the gas-phase enthalpy of formation for a large number of organic compounds at the standard state [ideal gas, 298 K conditions, referred to in what follows as $\Delta_f H°(298.15\ K)$ or simply $\Delta_f H°$]. Since the early compilation of experimentally derived radical enthalpy of formation data by O'Neal and Benson,[7] there have been other updated compilations (e.g., refs 8−10). Two more recent ones are the review by Sablier and Fujii[11] and the handbook of bond dissociation energies by Luo.[12] It should be pointed out that not all these reported data are obtained by direct experimental means, being sometimes derived from other measured data, obtained from correlations and/or by using computational methods. Nonetheless a sizable fraction of the data can be traced to experimental measurements using various kinetic or mass spectrometric methods. Another convenient data source is the Internet site NIST Chemistry WebBook[13] that provides a wealth of gas-phase thermochemical properties data such as standard state gas-phase enthalpy of formation for molecular species, radicals, and ions.

Despite the expanding availability of the experimental data, the database for the enthalpy of formation of the radicals, however, is still far from being comprehensive. The chance of stumbling upon radicals with no measured data being available (or one with a doubtful value) is much more real than in the

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case of the molecules. For instance, in connection with an attempt to calculate the enthalpy changes for various elementary reaction steps in the reaction mechanism postulated for the decomposition of cumene hydroperoxide and di-*tert*-butyl peroxide, one comes across a number of free radicals for which no data were reported.

Various group-additivity (GA) methods are available[14−16] for estimating enthalpies of formation of molecules. An alternative bond-additivity method and the so-called difference method are also available[15] for the same purpose. The group-additivity method developed by Benson and co-workers[17,18] is probably among the most suited for routine practical use considering the demonstrated applicability to a large number of compounds and the accuracy of the prediction. In this method, a group is defined as "a polyvalent atom (ligancy ≥ 2) in a molecule together with all of its ligands". A group is written as $X-(A)_i(B)_j(C)_k(D)_l$ where X is the central atom attached to *i* A atoms, *j* B atoms, etc. The groups and the associated contributions or the so-called group-additivity values (GAVs) in the case of molecules have been estimated exhaustively. Benson[19] later tabulated GAVs for 37 hydrocarbon groups, 61 oxygen-containing groups, 59 nitrogen-containing groups, 46 halogen-containing groups, 53 sulfur-containing groups, 57 organometallic groups, and 65 organophosporous and organoboron groups. In addition, there are corrections for nonbonded interactions that are somewhat empirically established. These were later updated by Cohen and Benson.[15]

A much simpler method based on bond additivities, while not nearly as accurate as the GA method, can be of use in the estimation of properties of molecules possessing unusual groups whose values have not yet been determined. Cohen and Benson[15] illustrated the method by deriving the bond-additivity values (BAVs) for enthalpy of formation for the C−H, C−C, C−O, and O−H bonds. It should be stressed that these values are not the same as the bond dissociation energy of the respective bonds. However, the method is not reliable in case of heavy branching. Also, in view of the limited availability of the data on BAVs, this method has not seen much application.

An estimation procedure that uses bond dissociation energy (BDE) values and sometimes offers a more accurate estimating scheme is the difference method (DM). This is most useful when one knows the enthalpy of formation of a molecule structurally very similar to that in which one is interested. Cohen[20] had demonstrated the use of this method for estimating the $\Delta_f H°$ of certain alkyl radicals.

Constantinou and Gani[16] presented a new group contribution approach to calculate various properties of pure compounds including enthalpy of formation by using the so-called first- and second-order group contributions. They compared their method with Benson's (GA) method and have claimed only a marginal improvement in accuracy in predicted enthalpy of formation of molecules over the GA method (older group-additivity values[17] seem to have been used in the above comparison). Moreover, applicability of this method to a wide variety of species, especially radicals with which we will be mainly concerned with in this paper, has not been tested.

In this context, it was decided to systematically re-evaluate a useful procedure such as the Benson's GA method for a consistent and wider applicability to the estimation of $\Delta_f H°$ for radicals. Unlike in the case of the molecular species for which the estimates by the GA method have been compared extensively with a large number of experimental data,[14,17] no such systematic comparison seems to have been made for radicals. This can, at least partially, be remedied now in view of the recently available data compilations referred to above. Apart from predicting unmeasured properties for radical species of interest, the estimates can also be used to cross check the reasonableness of the published data.

Although the database of GAVs for applying Benson's GA method to molecules is quite extensive, this is not the case with the free radical species. Estimation of radical enthalpy of formation has often been limited in the past due to nonavailability of reliable values of many required GAVs. In this work, we aim to show that the estimates of enthalpy of formation of a fairly large number of alkyl and oxygen-containing radicals that we obtained by the GA method are reliable and within the usual experimental error limit. This has been contingent upon our being able to devise simple methodologies to evaluate the GAVs for a number of unknown groups and to re-evaluate others for some of the existing groups. Similar methodologies can be extended to other radicals. Finally, we use some of these newly evaluated groups to estimate the enthalpy of formation for a number of radicals involved in the elementary reaction steps in the mechanism of a typical decomposition reaction cited in the literature. This allowed the prediction of enthalpy changes associated with the overall reaction.

Estimation of GAVs for the Radical Groups for the Benson GA Method: Previous Work

O'Neal and Benson[7] presented a general discussion on the free radical thermochemistry, reviewing the various experimental techniques for measurement as well as the GA-based estimation method for predicting the thermochemical properties. They presented GAVs for 45 radical groups. Some of these values were revised or updated in Benson's seminal work *Thermochemical Kinetics*.[19] As stated in the review by Cohen and Benson,[15] most of these GAVs have not been systematically revised since then except for some sporadic attempts.[20,21] Recently, Luo[12] has provided a more extended listing of GAVs pertinent to C/H, O/C/H, and N/C/H/O radicals, which included a number of updates by Cohen[22] and several new ones presented by the author without mentioning how these were obtained.

On a careful perusal of these GAVs, one becomes aware that a number of them are probably mere assignments to the values for the corresponding molecular group values. There are some groups especially pertinent to the oxygen-containing radicals, such as $O-(O^\bullet)(C)$ for which this may result in incorrect enthalpy of formation values. The GAV estimation method based on the experimental BDE data is a valid (though an indirect) one, except that one should be aware that there are variations in the BDE values[12] for the same class of bond occurring in different compounds having different neighboring atoms in varying bond combinations. Thus there is apparently a scope and a need to evaluate some of these groups independently.

The GAVs for free radicals, in the work of Benson and co-workers[7,15] were based on a minimum set of then well-established experimental data. In view of more recent and extensive compilations of radical enthalpy of formation data,[9−11] a direct estimation of the GAVs seem quite feasible.

Dilling[23] observed (and tested for about 90 odd data sets) an apparently linear correlation between the differences in Benson's GAVs for the free radical $\Delta_f H°$, namely, $\{[C^\bullet-(X)(Y)(Z)] - [C^\bullet-(H)(Y)(Z)]\}$ and for the related molecules, $\{[C-(H)(X)(Y)(Z)] - [C-(H)_2(Y)(Z)]\}$, expressed as follows:

$$[C^\bullet-(X)(Y)(Z)] - [C^\bullet-(H)(Y)(Z)] = \text{slope} \times \{[C-(H)(X)(Y)(Z)] - [C-(H)_2(Y)(Z)]\} + \text{intercept} \quad (2)$$

Table 1. Corresponding Groups Required To Calculate the GAVs for the Unknown Radical-Centered Alkyl Groups

unknown group	[$C^\bullet$−(X)(Y)(Z)]	[$C^\bullet$−(H)(Y)(Z)]	[C−(H)(X)(Y)(Z)]	[C−$(H)_2$(Y)(Z)]
$C^\bullet$−(C)$(H)_2$	$C^\bullet$−(C)(H)(H)	$C^\bullet$−(H)(H)(H)	C−(H)(C)(H)(H)	C−(H)(H)(H)(H)
$C^\bullet$−$(C)_2$(H)	$C^\bullet$−(C)(C)(H)	$C^\bullet$−(H)(C)(H)	C−(H)(C)(C)(H)	C−(H)(H)(C)(H)
$C^\bullet$−$(C)_3$	$C^\bullet$−(C)(C)(C)	$C^\bullet$−(H)(C)(C)	C−(H)(C)(C)(C)	C−(H)(H)(C)(C)

where the terms in square brackets denote GAVs for the enclosed radical or the molecular groups (in the units of kJ·mol^{-1}). The slope (dimensionless) has a mean value 0.857 and a standard deviation 0.031 while the intercept has a mean value of −19.41 kJ·mol^{-1} and a standard deviation 2.59 kJ·mol^{-1}. That is, replacing H atom ligand in a radical with some other ligand, X, is energetically almost equivalent to replacing one of two H ligands in a molecule with the same X ligand. X could be any among the following: C, C_B, C_d, C_t, CN, CO, Br, Cl, F, I, NO, O, Si, and Y; Z = H or the same X atoms or groups except Si. In general, many more group values are known for the molecular species than for the radicals, and the chances of knowing group values for simpler radicals are better than for complex radicals. This provided a way to estimate unknown radical group values when three other group values in the above correlation were known. It was used to derive new GAVs for some three-dozen groups not previously evaluated. However, no comparisons with the experimental data were provided so that the utility and/or limitation, if any, of this apparently useful correlation have not been examined.

In what follows, we shall demonstrate simple methodologies, which are essentially derived from this prior art for consistent evaluation of the GAVs. The latter will then be used to estimate the enthalpy of formation for a number of alkyl and oxygen-containing radicals. The estimated values will be compared with the reported data.

New Methodologies for the Evaluation of the Radical GAVs

Alkyl Radicals. There are two classes of radical groups: radical-centered groups such as [$C^\bullet$−(C)$(H)_2$] and radical-adjacent groups such as [C−($C^\bullet$)$(H)_3$]. Every radical with more than one group contains one of the former and at least one of the latter groups. Vis-à-vis the alkyl radicals there are a total of seven groups out of which three are radical-centered and four are radical-adjacent ones. The GAVs for the seven groups are defined as:

$$a = [\mathrm{C}^\bullet{-}(\mathrm{C})(\mathrm{H})_2]$$

$$b = [\mathrm{C}^\bullet{-}(\mathrm{C})_2(\mathrm{H})]$$

$$c = [\mathrm{C}^\bullet{-}(\mathrm{C})_3]$$

$$d = [\mathrm{C}{-}(\mathrm{C}^\bullet)(\mathrm{H})_3]$$

$$e = [\mathrm{C}{-}(\mathrm{C}^\bullet)(\mathrm{C})(\mathrm{H})_2]$$

$$f = [\mathrm{C}{-}(\mathrm{C}^\bullet)(\mathrm{C})_2(\mathrm{H})]$$

$$g = [\mathrm{C}{-}(\mathrm{C}^\bullet)(\mathrm{C})_3]$$

Cohen and Benson[15] [in the interest of brevity this reference will be denoted in future citations as CB92] had recalculated the above seven GAVs based on the experimental enthalpy of formation data for the following chosen set of radicals, namely, methyl, ethyl, isopropyl, *n*-propyl, *sec*-butyl, *tert*-butyl, and neopentyl (to be referred to henceforth, for the sake of brevity, as the basis radicals). They formed seven equations to calculate the GAVs: *a* through *g*. But, as pointed out therein, only six of these seven equations are linearly independent. So one of the seven group values had to be assigned arbitrarily. They assigned C−($C^\bullet$)$(H)_3$ = C−(C)$(H)_3$ and based on this assumption estimated the other six group values using the remaining equations.

To overcome the problem of insufficient equations to evaluate the GAVs, we have devised in this work a new methodology that does not require the arbitrary assumption that the earlier workers had made. Noting that Dilling[23] observed a good correlation among pairs of radical-centered groups we decided to use the same to calculate the GAVs for the three radical-centered groups, namely, *a*, *b*, and *c*. These three having been calculated by three independent equations, for the remaining four radical-adjacent groups we formulated four equations using the $\Delta_f H°$ value for four chosen basis radicals. The latter step was carried out in two ways. In the first case, we chose the same basis radicals as those used in CB92, while in the other case we have replaced two radicals used earlier by two new basis radicals. The data we have used here are obtained with different techniques (mostly mass spectrometric) and presumably have less reported uncertainty than the data used in the earlier evaluation.

Estimation of the Radical-Centered GAVs by Dilling's Correlation. The three radical-centered groups can be evaluated based on experimental values of $\Delta_f H°$ for an alkane, the corresponding alkyl radical and the pertinent molecular group values, if required. For instance, to calculate the GAV of $C^\bullet$−(C)$(H)_2$, we set

$$[\mathrm{C}^\bullet{-}(\mathrm{X})(\mathrm{Y})(\mathrm{Z})] \rightarrow [\mathrm{C}^\bullet{-}(\mathrm{C})(\mathrm{H})(\mathrm{H})] = a$$

$$[\mathrm{C}^\bullet{-}(\mathrm{H})(\mathrm{Y})(\mathrm{Z})] \rightarrow [\mathrm{C}^\bullet{-}(\mathrm{H})(\mathrm{H})(\mathrm{H})] = 146.56\ \mathrm{kJ{\cdot}mol^{-1}}\,{}^{38}$$

$$[\mathrm{C}{-}(\mathrm{H})(\mathrm{X})(\mathrm{Y})(\mathrm{Z})] \rightarrow [\mathrm{C}{-}(\mathrm{H})(\mathrm{C})(\mathrm{H})(\mathrm{H})] = -41.84\ \mathrm{kJ{\cdot}mol^{-1}}\,{}^{15}$$

$$[\mathrm{C}{-}(\mathrm{H})_2(\mathrm{Y})(\mathrm{Z})] \rightarrow [\mathrm{C}{-}(\mathrm{H})_2(\mathrm{H})(\mathrm{H})] = -74.87\ \mathrm{kJ{\cdot}mol^{-1}}\,{}^{13}$$

Then substituting above four values in eq 2, we calculated *a*, and a similar procedure was followed to calculate *b* and *c*. Table 1 shows the radical-centered groups and the three corresponding groups required to calculate the GAVs.

Estimation of the Radical-Adjacent GAVs. The four equations for the radical-adjacent groups were formulated taking isobutyl (i-Bu), *n*-propyl (n-Pr), *tert*-butyl (t-Bu), and neopentyl (neo-Pn) as the basis radicals. Table 2 shows that the precision in the data for the basis radicals in present work is better than in the earlier work while the values themselves are almost identical. For the same reason, for t-Bu we chose a value used earlier by Benson and co-workers (quoted by Cohen[20]) and which also appears in the latest compilation of $\Delta_f H°$ data based on mass spectrometry.[11]

Table 2. Comparison of Experimental Enthalpy of Formation ($\Delta_f H°$) Data for the Basis Radicals Used by Benson and Co-workers and Those Used in the Present Work for Estimation of the GAVs for the Alkyl Groups

	Benson's data			data used in the present work		
	$\Delta_f H°$		precision (±)	$\Delta_f H°$		precision (±)
radical	$kJ\cdot mol^{-1}$	ref	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	ref	$kJ\cdot mol^{-1}$
methyl	146.86	15	0.63	146.56	38	0.38
ethyl	118.83	15	2.09			
n-propyl	97.91	15	4.18	94.98	39	1.67
isopropyl	87.86	15	4.18			
isobutyl	66.94	15	4.18	66.11	39	1.25
sec-butyl	66.94	15	4.18			
tert-butyl	46.02	15	6.28	39.75	39	0.84
neopentyl	38.49	15	4.18	42.26	39	1.25
spiropentyl				380.45	10	3.99
cyclopentyl				107.03	12, 40	2.51
average			3.74			1.70

Table 3. Comparison of GAVs for the Alkyl Radicals

		present work	
	Cohen and Benson[15]	old basis	new basis
group	$GAV/(kJ\cdot mol^{-1})$	$GAV/(kJ\cdot mol^{-1})$	$GAV/(kJ\cdot mol^{-1})$
$[C^\bullet-(C)(H)_2]$	160.67	155.44	155.44
$[C^\bullet-(C)_2(H)]$	171.54	153.96	153.96
$[C^\bullet-(C)_3]$	171.54	143.87	143.87
$[C-(C^\bullet)(H)_3]$	−41.84	−34.71	−34.71
$[C-(C^\bullet)(C)(H)_2]$	−20.92	−18.63	−17.40
$[C-(C^\bullet)(C)_2(H)]$	−10.04	−5.65	−5.65
$[C-(C^\bullet)(C)_3]$	3.35	12.34	20.04

The four equations for the radical-adjacent groups are

$$d = [\Delta_f H°(\text{t-Bu}) - c]/3 \qquad (3)$$

$$e = \Delta_f H°(\text{n-Pr}) - a - [C-(C)(H)_3] \qquad (4)$$

$$f = \Delta_f H°(\text{i-Bu}) - a - 2[C-(C)(H)_3] \qquad (5)$$

$$g = \Delta_f H°(\text{neo-Pn}) - a - 3[C-(C)(H)_3] \qquad (6)$$

In eqs 3 to 6, a term like $[C-(C)(H)_3]$ denotes the GAV for the $C-(C)(H)_3$ group. With these equations, we calculated the GAVs for the radical groups *d* through *g*.

Now in a bid to broad base the basis radicals we replaced two of them, namely, the *n*-propyl and the neopentyl by two new radicals involving ring structures (i.e., cyclopentyl (cy-Pn) and spiropentyl (sp-Pn)) never used before in GAV evaluation. Equations for *d* and *f* remain the same, and the equations to calculate *e* and *g* are as follow:

$$e = \{\Delta_f H°(\text{cy-Pn}) - b - 2[C-(C)_2(H)_2] - (\text{cyclopentane\_correction})\}/2 \qquad (7)$$

$$g = \Delta_f H°(\text{sp-Pn}) - b - e - 2[C-(C)_2(H)_2] - (\text{spiropentane\_correction}) \qquad (8)$$

All molecular GAVs required in these equations are taken from CB92. The GAVs *a* through *g* newly evaluated in the present work using both the old and the new set of basis radicals are tabulated in Table 3.

In the Results and Discussion section, we will use both these new sets of GAVs and those given in CB92 to predict $\Delta_f H°$ for a large number of alkyl radicals for which this property has been reported by one or more research groups. The predicted and the reported values will be compared.

Oxygen-Containing Radicals. Oxygen-containing free radicals mainly result from alcohols, ketones, aldehydes, ethers, and esters and also from hydroperoxides and peroxides. Due to the scarcity of experimental data for enthalpies of formation of these radicals, Benson's GA method can be useful in predicting the same. However, the lack of availability of the pertinent GAVs has limited the application of the method to only a few cases. Benson and Shaw[24] had originally assigned values to six oxygen-containing radical groups. These were later revised and updated[7,19] with the addition of three more groups containing the carbonyl ligand. Given the increasing availability of experimental $\Delta_f H°$ data on the oxygen-containing radicals over the years,[9−12] there seems to be a scope for evaluating new GAVs.

Table 4. Experimental Enthalpy of Formation ($\Delta_f H°$) Data for the Oxygen-Containing Basis Radicals

		$\Delta_f H°$	precision (±)	
no.	radical	$kJ\cdot mol^{-1}$	$kJ\cdot mol^{-1}$	ref
1	hydroxy methyl ($^\bullet CH_2OH$)	−17.78	1.26	41
2	propenoyl ($H_2C{=}CHC(O^\bullet)$)	241.42	8.37	42
3	2-hydroxy propyl ($C^\bullet H_2CHOHCH_3$)	−96.23	12.55	43
4	hydroxy *tert*-butyl ($^\bullet CH_2C(OH)(CH_3)_2$)	−147.28	12.55	43
5	1-hydroxy 2-propyl ($CH_3C^\bullet HCH_2OH$)	−78.66	12.55	43
6	$^\bullet CH_2C(O)OH$	−257.73	12.55	43
7	$CH_3C(O)O^\bullet$	−216.31	12.55	43
8	vinyloxy ($CH_2{=}CHO^\bullet$)	0.84	8.37	44
9	methoxy methyl ($CH_3OC^\bullet H_2$)	−11.69	5.00	8
10	$CH_3O(CO^\bullet)$	−168.91	4.00	43
11	$C_6H_5(CO^\bullet)$	109.13	8.00	8
12	phenoxy ($C_6H_5O^\bullet$)	47.66		8
13	$^\bullet CH_2CHO$	10.49	9.19	37
14	$CH_3\,C(O)C^\bullet HCH_3$	−70.25	7.10	8
15	$C_6H_5C(O)OC^\bullet H_2$	−69.85	8.37	8
16	$^\bullet CH_2C(O)CH_3$	−50.21	6.28	44
17	pimethoxy methyl ($(CH_3O)_2C^\bullet H$)	−184.93	8.37	42
18	1-hydroxy ethyl ($CH_3C^\bullet HOH$)	−63.55	4.18	8
19	$CH_2{=}CHC^\bullet HOH$	0.0		8
20	$(CH_3)_2C^\bullet OH$	−111.21	4.60	8

In this work, we distinguish two different categories of oxygen-containing radicals. The first involves the oxygenated alkyl radicals, namely, those resulting from the C−H bond breaking from alcohols, ketones, etc. as well as the alkoxy and phenoxy radicals that arise from the O−H bond breaking in alcohols and phenols. The second category mainly consists of the alkoxy and peroxy radicals arising from the hydroperoxides (i.e., by breaking the (RO−OH) or the (ROO−H) bonds).

GAVs Pertinent to Radicals Arising from the C−H Bond Breaking from Alcohols, Ketones, etc. and the O−H Bond Breaking in Alcohols and Phenols. From the published data of the oxygen-containing radicals,[9−11] we identified a list of 22 groups for the application of the GA method, for many of which the GAVs have not been estimated previously. In this work we proceeded to evaluate these.

Out of these 22 groups listed in Table 6, it is possible to evaluate the GAVs for nine of them from independent equations based on nine experimental data points since these equations

Table 5. Corresponding Groups Required To Calculate Unknown Radical-Centered Oxygen-Containing Groups

group	$[C^{\bullet}-(X)(Y)(Z)]$	$[C^{\bullet}-(H)(Y)(Z)]$	$[C-(H)(X)(Y)(Z)]$	$[C-(H)_2(Y)(Z)]$
$C^{\bullet}-(O)(H)_2$	$C^{\bullet}-(O)(H)(H)$	$C^{\bullet}-(H)(H)(H)$	$C-(H)(O)(H)(H)$	$C-(H)(H)(H)(H)$
$C^{\bullet}-(C)(H)(O)$	$C^{\bullet}-(C)(H)(O)$	$C^{\bullet}-(H)(H)(O)$	$C-(H)(C)(H)(O)$	$C-(H)(H)(H)(O)$
$C^{\bullet}-(Cd)(H)(O)$	$C^{\bullet}-(Cd)(H)(O)$	$C^{\bullet}-(H)(H)(O)$	$C-(H)(Cd)(H)(O)$	$C-(H)(H)(H)(O)$
$C^{\bullet}-(C)_2(O)$	$C^{\bullet}-(C)(C)(O)$	$C^{\bullet}-(H)(C)(O)$	$C-(H)(C)(C)(O)$	$C-(H)(H)(C)(O)$
$C^{\bullet}-(CO)(H)_2$	$C^{\bullet}-(CO)(H)(H)$	$C^{\bullet}-(H)(H)(H)$	$C-(H)(CO)(H)(H)$	$C-(H)(H)(H)(H)$
$C^{\bullet}-(C)(H)(CO)$	$C^{\bullet}-(C)(H)(CO)$	$C^{\bullet}-(H)(H)(CO)$	$C-(H)(C)(H)(CO)$	$C-(H)(H)(H)(CO)$
$C^{\bullet}-(H)(O)_2$	$C^{\bullet}-(O)(O)(H)$	$C^{\bullet}-(H)(O)(H)$	$C-(H)(O)(O)(H)$	$C-(H)(H)(O)(H)$

Table 6. GAVs for the Radical Groups Arising from the C−H Bond Breaking from Alcohols, Ketones, etc. and the O−H Bond Breaking in Alcohols Based on Two Different Approaches

		GAV/(kJ·mol^{-1})	
	group	approach 1	approach 2
G1	$C-(C^{\bullet})(H)_2(O)$	−39.55	−39.55
G2	$C-(C^{\bullet})(C)_2(O)$	−60.68	−60.68
G3	$CB-(O^{\bullet})$	−21.17	−21.17
G4	$CO-(O^{\bullet})(C)$	−174.47	−174.47
G5	$C-(C^{\bullet})(H)(C)(O)$	−51.47	−51.47
G6	$CB-(CO^{\bullet})$	40.30	40.30
G7	$O-(CO^{\bullet})(C)$	−127.07	−127.07
G8	$Cd-(CO^{\bullet})(H)$	215.18	215.18
G9	$Cd-(O^{\bullet})(H)$	−25.40	−25.40
G10	$C^{\bullet}-(C)(H)(O)$	142.84	117.40
G11	$C^{\bullet}-(O)(H)_2$	155.44	128.47
G12	$C^{\bullet}-(Cd)(H)(O)$	147.14	84.08
G13	$C^{\bullet}-(C)_2(O)$	126.65	104.45
G14	$C^{\bullet}-(CO)(H)_2$	155.44	124.26
G15	$C^{\bullet}-(CO)(H)(C)$	153.24	138.93
G16	$C^{\bullet}-(H)(O)_2$	112.00	95.39
G17	$O-(C^{\bullet})(C)$	−125.30	−98.32
G18	$CO-(C^{\bullet})(C)$	−146.94	−132.63
G19	$CO-(C^{\bullet})(O)$	−170.51	−139.33
G20	$CO-(C^{\bullet})(H)$	−144.95	−113.77
G21	$O-(C^{\bullet})(CO)$	−156.47	−129.49
G22	$O-(C^{\bullet})(H)$	−173.22	−146.25

have only one unknown group. For these equations, we have chosen the experimental values with minimum uncertainty in terms of the quoted deviation from the mean value. The basis radicals used to calculate the GAVs are tabulated in Table 4:

$$G1 = \Delta_f H°(CH_3C^{\bullet}HCH_2OH) - d - b - [O-(C)(H)] \quad (9)$$

$$G2 = \Delta_f H°(^{\bullet}CH_2C(OH)(CH_3)_2) - 2[C-(C)(H)_3] - a - [O-(C)(H)] \quad (10)$$

$$G3 = \Delta_f H°(C_6H_5O^{\bullet}) - 5[CB-(H)] \quad (11)$$

$$G4 = \Delta_f H°(CH_3C(O)O^{\bullet}) - [C-(CO)(H)_3] \quad (12)$$

$$G5 = \Delta_f H°(^{\bullet}CH_2CHOHCH_3) - [C-(C)(H)_3] - a - [O-(C)(H)] \quad (13)$$

$$G6 = \Delta_f H°(C_6H_5(CO)^{\bullet}) - 5[CB-(H)] \quad (14)$$

$$G7 = \Delta_f H°(CH_3O(CO)^{\bullet}) - [C-(O)(H)_3] \quad (15)$$

$$G8 = \Delta_f H°(H_2C{=}CH(CO^{\bullet})) - [Cd-(H)] \quad (16)$$

$$G9 = \Delta_f H°(H_2C{=}CHO^{\bullet}) - [Cd-(H)_2] \quad (17)$$

Each of the above set of nine equations (eqs 9 to 17) contains only one unknown group. The calculated GAVs for these groups from G1 through G9 are presented in Table 6. The remaining groups in the equations are the known Benson's molecular groups (CB92) and the updated alkyl groups (*a* to *g*) evaluated in this paper. Once these nine groups G1 through G9 became known, we took either one of the two following approaches to calculate the remaining 13 groups (i.e., G10 through G22).

Approach 1. In this approach, we divided these 13 groups (G10 to G22) into two categories, namely, the radical-centered groups and the radical-adjacent groups. For the seven radical-centered groups (G10 to G16), we used Dilling's correlation (eq 2) as we did in the case of the alkyl radicals. For the remaining six radical-adjacent groups, we formulated equations based on the experimental data and used GAVs of already evaluated radical groups. The molecular GAVs, as usual, were taken from CB92. For instance, to calculate the GAV for $C^{\bullet}-(O)(H)_2$ we set

$$[C^{\bullet}-(X)(Y)(Z)] \rightarrow [C^{\bullet}-(O)(H)(H)] = G10$$

$$[C^{\bullet}-(H)(Y)(Z)] \rightarrow [C^{\bullet}-(H)(H)(H)] = 146.56\ \text{kJ·mol}^{-1}\ ^{38}$$

$$[C-(H)(X)(Y)(Z)] \rightarrow [C-(H)(O)(H)(H)] - 41.84\ \text{kJ·mol}^{-1}\ ^{15}$$

$$[C-(H)_2(Y)(Z)] \rightarrow [C-(H)(H)(H)(H)] = -74.87\ \text{kJ·mol}^{-1}\ ^{13}$$

Then substituting the above four values in eq 2, we calculated the GAV for the group G10, and a similar procedure was followed for the groups G11 to G16 by forming seven independent equations. Table 5 shows the radical-centered groups and the corresponding groups required to calculate their values.

Next we formulated the equations for the six radical-adjacent groups (G17 to G22) based on the experimental data (as reported in the Table 4) as follows:

$$G17 = \Delta_f H°(CH_3OC^{\bullet}H_2) - [C-(O)(H)_3] - G11 \quad (18)$$

$$G18 = \Delta_f H°(CH_3C(O)C^{\bullet}HCH_3) - [C-(CO)(H)_3] - d - G15 \quad (19)$$

$$G19 = \Delta_f H°(^{\bullet}CH_2C(O)OH) - [O-(CO)(H)] - G14 \quad (20)$$

$$G20 = \Delta_f H°(^{\bullet}CH_2CHO) - G14 \quad (21)$$

$$G21 = \Delta_f H°(C_6H_5C(O)OC^{\bullet}H_2) - 5[CB-(H)] - [CB-(CO)] - [CO-(CB)(O)] - G11 \quad (22)$$

$$G22 = \Delta_f H°(^{\bullet}CH_2OH) - G11 \quad (23)$$

The GAVs for G10 through G22 are then tabulated in Table 6. We have also used another approach to calculate these GAVs as described below.

Approach 2. In this approach, we do not make any distinction between the radical-centered and the radical-adjacent groups. Here we formulated 13 equations for the 13 groups G10 to G22 using the reported experimental data. But the problem in doing so is that two of these equations are not linearly independent. To overcome this problem, we have made an assumption similar to what Cohen and Benson[15] did in their re-evaluation of the GAVs for the alkyl radicals. Assuming that G17 = $[O-(C^{\bullet})(C)] = [O-(C)_2] = -98.32$ kJ·mol^{-1} and G18 = $[CO-(C^{\bullet})(C)] = [CO-(C)_2] = -132.63$ kJ·mol^{-1}, the other 11 GAVs can be calculated from the experimental $\Delta_f H°$ data for the basis radicals. The relationships are as follows:

$$G11 = \Delta_f H°(CH_3OC^{\bullet}H_2) - [C{-}(O)(H)_3] - G17 \quad (24)$$

$$G22 = \Delta_f H°(^{\bullet}CH_2OH) - G11 \quad (25)$$

$$G10 = \Delta_f H°(CH_3C^{\bullet}HOH) - d - G22 \quad (26)$$

$$G12 = \Delta_f H°(CH_2{=}CHC^{\bullet}HOH) - [Cd{-}(H)_2] - [Cd{-}(C^{\bullet})(H)] - G22 \quad (27)$$

$$G13 = \Delta_f H°((CH_3)_2C^{\bullet}OH) - 2d - G22 \quad (28)$$

$$G16 = \Delta_f H°((CH_3O)_2C^{\bullet}H) - 2[C{-}(O)(H)_3] - 2 \times G17 \quad (29)$$

$$G15 = \Delta_f H°(CH_3C(O)C^{\bullet}HCH_3) - [C{-}(CO)(H)_3] - d - G18 \quad (30)$$

$$G14 = \Delta_f H°(^{\bullet}CH_2C(O)CH_3) - [C{-}(CO)(H)_3] - G18 \quad (31)$$

$$G19 = \Delta_f H°(^{\bullet}CH_2C(O)OH) - [O{-}(CO)(H)] - G14 \quad (32)$$

$$G21 = \Delta_f H°(C_6H_5C(O)OC^{\bullet}H_2) - 5[CB{-}(H)] - [CB{-}(CO)] - [CO{-}(CB)(O)] - G11 \quad (33)$$

$$G20 = \Delta_f H°(^{\bullet}CH_2CHO) - G14 \quad (34)$$

Equations 24 to 34 along with the two assignments for G17 and G18 evaluated the GAVs for the groups G10 through G16 and G19 through G22. These values are also listed in Table 6.

The GAVs obtained by these two approaches were used to predict the enthalpies of formation of a number of oxygen-containing radicals. Comparison of the predicted values with the $\Delta_f H°$ data reported by different research groups will be made under the Results and Discussion section.

GAVs Pertinent to (the Alkoxy and Peroxy) Radicals Arising from Breaking of the (RO−OH) and the (ROO−H) Bonds in Hydroperoxides. Some of the groups required in this context were the first few oxygen-containing radical groups, such as $O{-}(O^{\bullet})(C)$, evaluated by Benson and Shaw.[24] The procedure adopted for calculating the GAVs for this subcategory of the oxygen-containing radical groups is different from that used above and is based on the data on BDE for the ROOH bond breaking reaction or $\Delta_f H°$ for the corresponding $RO^{\bullet}$ or $ROO^{\bullet}$ radical. While published data in the literature are sometimes indirectly derived ones (sometimes even estimated ones), we have tried to use published experimental data as far as possible. The following radical groups will be considered for illustrating the procedure:

1. $[C{-}(CB)(C)_2(O^{\bullet})] = G23$
2. $[O{-}(O^{\bullet})(C)] = G24$
3. $[O{-}(O^{\bullet})(CO)] = G25$

1. [C−(CB)(C)₂(O•)] = G23. This group occurs in the cumyloxy radical, which is typical of the substituted benzyloxy ($RO^{\bullet}$) radicals. The required GAV can be back-calculated from the known value of $\Delta_f H°$ for the said radical (i.e., $C_6H_5C(CH_3)_2O^{\bullet}$, which has been reported[25] as 71.13 kJ·mol^{-1}). Contributions by various constituent groups to the enthalpy of formation of this radical are as follows:

$$[CB{-}(H)] = (5) \times \{13.77\} = 68.85 \text{ kJ·mol}^{-1}$$

$$[CB{-}(C)] = (1) \times \{22.97\} = 22.97 \text{ kJ·mol}^{-1}$$

$$[C{-}(C)(H)_3] = (2) \times \{-41.84\} = -83.68 \text{ kJ·mol}^{-1}$$

$$[C{-}(CB)(C)_2(O^{\bullet})] = (1) \times \{G23\} = G23 \text{ kJ·mol}^{-1}$$

The sum of the above four group contributions should be equal to 71.13 kJ·mol^{-1}. The number included within the curly bracket is the GAV of a group (molecular ones as per CB92), and that appearing within the parenthesis is the frequency of its occurrence in the radical. G23 is the only unknown parameter in this relationship. Hence

$$G23 = [C{-}(CB)(C)_2(O^{\bullet})] = 62.99 \text{ kJ·mol}^{-1}$$

2. [O−(O•)(C)] = G24. This group is an ubiquitous one that occurs in the peroxy radical groups ($ROO^{\bullet}$) associated with a number of alkyl and benzylic $R^{\bullet}$. G24 can be calculated from the reported bond dissociation energy, $D°(ROO{-}H)$, for breaking the (ROO−H) bond that dissociates (taking benzyl hydroperoxide as an example) as

$$C_6H_5C(H_2)OOH \rightarrow C_6H_5C(H_2)OO^{\bullet} + H^{\bullet}$$

Taking $D°(ROO{-}H)$ as 363.17 kJ·mol^{-1} as reported by Jonsson,[45] we could calculate the $\Delta_f H°$ of the corresponding $ROO^{\bullet}$ (benzyl peroxy) radical. In doing so, $\Delta_f H°$ for benzyl hydroperoxide was calculated by Benson's group contribution method (as no experimental data are available) using the known molecular groups. That for the hydrogen radical was taken to be 217.99 kJ·mol^{-1},[24] i.e.

$$\Delta_f H°(ROO^{\bullet}) = D°(ROO{-}H) - \Delta_f H°(H^{\bullet}) + \Delta_f H° \,(ROOH)$$

$$= (363.17 - 217.99 - 29.12) \text{ kJ·mol}^{-1}$$

$$= 116.06 \text{ kJ·mol}^{-1}$$

It is to be noted that $\Delta_f H°$ for this $ROO^{\bullet}$ group has been independently reported as 114.64 kJ·mol^{-1},[46] which is indeed very close to the calculated value. This provides at least a partial justification for the above procedure. Now using this value, we back-calculated the GAV for the unknown group (i.e., G24). For the benzyl peroxy radical, the $\Delta_f H°$ calculation could be set up as follows:

$$[CB{-}(H)] = (5) \times \{13.77\} = 68.85 \text{ kJ·mol}^{-1}$$

$$[CB{-}(C)] = (1) \times \{22.97\} = 22.97 \text{ kJ·mol}^{-1}$$

$$[C{-}(CB)(H)_2(O)] = (1) \times \{-33.89\} = -33.89 \text{ kJ·mol}^{-1}$$

$$[O{-}(O^{\bullet})(C)] = (1) \times \{G24\} = G24 \text{ kJ·mol}^{-1}$$

The sum of the above four group contributions should be equal to 116.06 kJ·mol^{-1}. Given the values for the other known molecular groups, G24 is the only unknown parameter in this relationship. This leads to

$$G24 = [O{-}(O^{\bullet})(C)] = 58.13 \text{ kJ·mol}^{-1}$$

It should be noted that Benson and Shaw[24] gave this group value as 75.31 kJ·mol^{-1} based on $D°(ROO{-}H) \approx D°($HOO−

Table 7. GAVs for the (Alkoxy and Hydroperoxy) Radicals Arising from Breaking of the (RO−OH) and the (ROO−H) Bonds in Hydroperoxides

	group	GAV/(kJ·mol^{-1})
G23	$C-(CB)(C)_2(O^\bullet)$	62.99
G24	$O-(O^\bullet)(C)$	51.04
G25	$O-(O^\bullet)(CO)$	20.63

H) = 376.56 kJ·mol^{-1}. As we shall see in light of the arguments presented under the Results and Discussion section, the G24 value may require a further modification. The recommended value is 51.04 kJ·mol^{-1}.

3. [O−(O•)(CO)] = G25. Consider the dissociation of methaneperoxycarboxylic acid:

$$CH_3C(O)OOH \rightarrow CH_3C(O)OO^\bullet + H^\bullet$$

$D°$(ROO−H) has been reported to be 386.18 kJ·mol^{-1}.[45] Using this value, we calculated the $\Delta_f H°$ of ROO$^\bullet$ radical from that of the parent compound (ROOH), −336.69 kJ·mol^{-1} (again calculated by Benson's group contribution procedure as no experimental data are available) and of the hydrogen radical (217.99 kJ·mol^{-1}):

$$\Delta_f H°(ROO^\bullet) = D°(ROO-H) - \Delta_f H°(H^\bullet) + \Delta_f H°(ROOH)$$

$$= (386.18 - 217.99 - 336.69)\ \text{kJ·mol}^{-1}$$

$$= -168.50\ \text{kJ·mol}^{-1}$$

The corresponding reported value[47] is −171.96 kJ·mol^{-1}. Now, for the ROO$^\bullet$ radical, group assignment for the $\Delta_f H°$ calculation can be made as it was done for G24. From the relationship involving the known molecular GAVs and value for $\Delta_f H°$(ROO$^\bullet$), the only unknown group [O−(O$^\bullet$)(CO)] was evaluated as

$$G25 = [O-(O^\bullet)(CO)] = 20.63\ \text{kJ·mol}^{-1}$$

The GAVs for groups G23 through G25 as calculated above are listed in Table 7.

Results and Discussion

Validity of the Newly Estimated GAVs for the Alkyl Radical Groups. Table 8 compares the predicted values for $\Delta_f H°$ for a number of alkyl radicals calculated by using the GAVs listed in CB92 and the two new sets of GAVs obtained in this work (see Table 3) against experimental data from one compilation.[11] In Table 9, similar comparisons are made against the data from the *CRC Handbook*.[10] Most of the data reported in these two compilations are based on experimental measurements involving either various mass spectrometric techniques or the kinetic methods. However, it will be well to be aware that a small number of data (especially reported in the *CRC Handbook*) may be indirectly derived, estimated, or evaluated otherwise. Given the GAV estimates provided in this work, it was our purpose to be able to estimate $\Delta_f H°$ for as many radicals as are normally listed in accessible and standard compilations and compare the predictions against the reported values. Once the primary validation is done here, one would be free to test the validity and efficacy of the proposed GAVs against more unimpeachable and varied primary data sources and update them if necessary in the future.

It should be pointed out with reference to the results presented in these tables that, for some radicals, multiple data (with varying quoted precision) sourced from a number of original publications (as compiled in these two sources) have been considered. Also, the specific $\Delta_f H°$ data used for the basis radicals (listed in Table 2) in order to evaluate the GAVs by a particular approach (old basis or new basis) were excluded for the comparison of results obtained by the same approach. This is signified by a blank cell in Tables 8 and 9. Δ is defined as the absolute difference between the mean experimental value and the calculated one.

It can be inferred from Tables 8 and 9 that the average absolute numerical difference (Δ) obtained with the updated GAVs (using either the old or the new set of basis radicals) is comparable to the usual range of experimental precision of 4.2 to 6.3 kJ·mol^{-1} in the measured $\Delta_f H°$ data. Moreover, using either basis set, the predicted $\Delta_f H°$ is closer to the mean experimental value, on the average, than obtained by using the GAVs in CB92 and is characterized by a lower standard deviation (± 4.7 for the old basis and ± 4.4 for the new basis as against ± 5.5 for the CB92 basis). It can also be shown that the experimental versus predicted parity plots obtained with data using the GAVs from this work have as high a correlation coefficient (0.97) as obtained with the CB92 GAVs but with less offset from the 45° line. It may be added that, in the latest compilation of the GAVs by Luo,[12] the same values as reported in CB92 have been reproduced.

On the whole, it may be remarked that while the Benson GAVs gave comparable results for smaller and simpler alkyl radicals up to, say, butyl radical, for radicals with higher carbon numbers as well as branching (say, 2-pentyl, 2-hexyl, 2-methyl-2-pentyl, 2-methyl-2-hexyl) and also for cycloalkyl radicals (e.g., cyclobutyl, cyclopentyl, and cyclohexyl), the new GAVs (with old basis) gave much better results. Further results on $\Delta_f H°$ for higher and heavily branched alkyl radicals will be presented shortly.

Validity of the Newly Estimated GAVs for the Oxygen-Containing Radical Groups. The comparison of the predicted enthalpies of formation of oxygen-containing free radicals using the new GAVs (see Tables 6) with the experimental data from two different sources as above are shown in Table 10. Additional GAVs for the pertinent alkyl radicals (old basis), as required, were taken from the present work. GAVs for the molecular groups, if any, were taken from CB92. The same comments about the nature and the limitation of the data, as well as the choice of multiple data for some radicals, as made above with regard to the alkyl radicals equally apply.

Table 10 clearly shows that the GAVs obtained by both approaches allow fairly accurate prediction of the pertinent radical $\Delta_f H°$ values (within the nomally expected precision of measured data such as 4.2 to 6.3 kJ·mol^{-1}) with approach 2 giving slightly better results than approach 1.

It may be noted that out of the 22 oxygen-containing groups considered in this work, GAVs for the groups G16 [$C^\bullet-(H)(O_2)$] and G19 [$CO-(C^\bullet)(O)$] have not appeared in the latest compilation by Luo,[12] thus being reported for the first time. For 13 groups, namely, G1 through G9, G17, G18, G20, and G21, the values reported by Luo[12] (in his Table 11.4.2) are same as those of the corresponding molecular groups as listed in CB92. For instance, for the group G1 [$C-(C^\bullet)(H)_2(O)$], the GAV reported by Luo[12] is −33.89 kJ·mol^{-1}, which happens to be the same as the one reported for the molecular group [$C-(C)(H)_2(O)$] in CB92. Similarly, for G8 [$Cd-(CO^\bullet)(H)$], the GAV reported[12] is 20.92 kJ·mol^{-1}, which is the same as reported in CB92 for the group [$Cd-(CO)(H)$]. The groups for which the GAVs seem to have been evaluated earlier are only seven, two of them (namely, G12 and G22) by Cohen[22] and the remaining five (G10, G11, G13, G14, and G15) by Luo,[12] presumably from

Table 8. Comparison of Predicted $\Delta_f H°$ of Alkyl Radicals with the Experimental Data[11]

			Benson's work		this work old basis		this work new basis	
radical	expt $\Delta_f H°$ kJ·mol⁻¹	precision (±) kJ·mol⁻¹	calcd $\Delta_f H°$ kJ·mol⁻¹	Δ^a kJ·mol⁻¹	calcd $\Delta_f H°$ kJ·mol⁻¹	Δ^a kJ·mol⁻¹	calcd $\Delta_f H°$ kJ·mol⁻¹	Δ^a kJ·mol⁻¹
ethyl	116.32	2.51	118.83	2.51	120.74	4.42	120.74	4.42
	120.92	1.67	118.83	2.09	120.74	0.18	120.74	0.18
1-propyl	94.98	1.67	97.91	2.93			96.21	1.23
isopropyl	79.91	2.51	87.86	7.95	84.55	4.64	84.55	4.64
	73.64	4.60	87.86	14.22	84.55	10.91	84.55	10.91
1-butyl	75.73	2.51	76.99	1.26	74.06	1.67	75.29	0.44
	71.13	5.02	76.99	5.86	74.06	2.93	75.29	4.16
2-butyl	75.73	2.51	66.94	8.79	58.79	16.94	60.02	15.71
	71.13	5.02	66.94	4.19	58.79	12.34	60.02	11.11
1-pentyl	42.26	1.26	56.07	13.81	53.14	10.88	54.37	12.11
neopentyl	42.26	1.26	38.49	3.77			49.96	7.70
2-pentyl	30.96	12.55	46.02	15.06	37.87	6.91	39.10	8.14
2-me,2-butyl	12.97	12.55	28.45	15.48	17.33	4.36	18.56	5.59
2-hexyl	12.55	12.55	25.10	12.55	16.95	4.40	18.18	5.63
2-me,2-pentyl	−7.95	12.55	7.53	15.48	−3.59	4.36	−2.36	5.59
2-me,2-hexyl	−27.61	12.55	−13.39	14.22	−24.51	3.10	−23.28	4.33
average		5.83		8.76		6.29		6.37

[a] Δ = absolute value (mean expt $\Delta_f H°$ − calcd $\Delta_f H°$).

Table 9. Comparison of Predicted $\Delta_f H°$ of Alkyl Radicals with the Experimental Data[10]

			Benson's work		this work old basis		this work new basis	
radical	expt $\Delta_f H°$ kJ·mol⁻¹	precision (±) kJ·mol⁻¹	calcd $\Delta_f H°$ kJ·mol⁻¹	Δ^a kJ·mol⁻¹	calcd $\Delta_f H°$ kJ·mol⁻¹	Δ^a kJ·mol⁻¹	calcd $\Delta_f H°$ kJ·mol⁻¹	Δ^a kJ·mol⁻¹
ethyl	120.82	1.59	118.83	1.99	120.74	0.08	120.74	0.08
1-propyl	97.45	2.50	97.91	0.46	94.98	2.47	96.21	1.24
isopropyl	89.94	1.59	87.86	2.08	84.55	5.39	84.55	5.39
neopentyl	36.38	7.99	38.49	2.11	42.26	5.88	49.97	13.59
2-me,2-butyl	32.18	6.32	28.45	3.73	17.33	14.85	18.56	13.62
spiropentyl	380.45	4.00	377.81	2.64	371.51	8.94		
cyclobutyl	214.06	4.18	220.91	6.85	207.92	6.14	210.38	3.68
cyclopentyl	107.03	2.51	117.57	10.54	104.57	2.46		
cyclohexyl	58.16	4.00	69.87	11.71	56.87	1.29	59.33	1.17
cycloheptyl	51.07	4.00	74.47	23.40	61.48	10.41	63.94	12.87
average		3.87		6.55		5.79		6.46

[a] Δ = absolute value (mean expt $\Delta_f H°$ − calcd $\Delta_f H°$).

the bond dissociation energy data. The reported values, though, are obviously different in magnitude from the GAVs evaluated in the present work considering that these were estimated by entirely different methods and utilizing different sources of data. Thus the GAVs for all the 22 groups taken together obtained by either of the two approaches presented in this work can be seen to provide a more consistent set of values for a wider set of oxygen-containing radical groups than reported so far.

Estimation of Enthalpies of Formation of Higher Alkyl Radicals. The GAVs for the alkyl radical groups were estimated in this work as well as by Benson and Cohen[15,20] by using basis radicals that are essentially low carbon number species. In various applications, however, one is more likely to encounter alkyl radicals generated from hydrocarbons with larger carbon numbers and/or those with significant branching. For such higher alkyl radicals, since experimental data are scarce, it is of interest to examine how well the GA method would estimate the $\Delta_f H°$. In the literature, apparently, there has been no such attempt.

One, however, comes across a rare attempt[20] along that line but using the so-called difference method originally used by O'Neal and Benson[7] in the context of the estimation of the other thermochemical properties such as entropy and specific heat. The method is based on the following assumption: if we know the enthalpy of formation of parent molecule (in the present context, say, the parent alkane) then by the fact that the enthalpy of reaction is the sum of the enthalpies of formation of all products minus the enthalpies of formation all reactants, we can calculate enthalpy of formation of radical taking bond dissociation energies (BDEs) as the enthalpy change for the relevant bond dissociation. Here one estimates the enthalpies of formation for radicals by assuming that BDEs are constant for each class of C−H bond: primary (420.5 ± 4.2) kJ·mol⁻¹, secondary (410.5 ± 6.3) kJ·mol⁻¹, and tertiary (398.3 ± 8.4) k J·mol⁻¹.

Cohen[20] had provided values for the enthalpies of formation (calculated on the above basis) for a number of alkyl radicals of this type. To test the efficacy of the GAVs estimated in this work for the same purpose, we did the estimation using the two sets of GAVs (from the Table 3). It should be noted that nonbonded (gauche) corrections were applied, wherever appropriate, for the heavily branched radaicals. The results are compared in the Table 11 with the values reported by Cohen. It appears that the GA method using the new GAVs can estimate the enthalpies of these branched higher alkyl radicals almost as closely as the difference method (to within ± 4.2 kJ·mol⁻¹).

The limitation of the difference method lies in the assumption of a constant BDE value for one category of C−H bond. According to Cohen[20] there is no certainty that this assertion is true, especially for higher or more highly branched alkyl radicals. Moreover, in absence of experimental data for the parent molecules, the GA method may have to be resorted to

Table 10. Comparison of Predicted $\Delta_f H°$ of the Oxygen-Containing Radicals with the Experimental Data

			approach 1		approach 2	
	expt $\Delta_f H°$	precision (±)	calcd $\Delta_f H°$	Δ^a	calcd $\Delta_f H°$	Δ^a
radical	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
hydroxy methyl ($^\bullet CH_2OH$)	−23.85[11]	8.37	−17.78	6.07	−17.78	6.07
	−24.27[11]	12.55	−17.78	6.49	−17.78	6.49
	−15.48[11]	2.93	−17.78	2.30	−17.78	2.30
	−20.50[11]		−17.78	2.72	−17.78	2.72
	−17.06[10]	3.30	−17.78	0.72	−17.78	0.72
1-hydroxy ethyl ($CH_3C^\bullet HOH$)	−65.27[11]		−65.09	0.18	−63.55	1.72
	−74.06[11]	8.37	−65.09	8.97	−63.55	10.51
	−60.67[11]	12.55	−65.09	4.42	−63.55	2.88
	−63.55[10]	4.18	−65.09	1.54		
2-hydroxy ethyl ($^\bullet CH_2CH_2OH$)	−36.40[11]	8.37	−42.47	6.07	−42.47	6.07
	−56.48[11]	12.55	−42.47	14.01	−42.47	14.01
methoxy methyl ($CH_3OC^\bullet H_2$)	−8.79[11]	8.37	−11.69	2.90	−11.69	2.90
	−5.44[11]	8.37	−11.69	6.25	−11.69	6.25
1-ethyl methoxy ($CH_3C^\bullet HOCH_3$)	−57.74[11]	8.37	−59.00	1.26	−57.47	0.27
1,2-dihydroxy ethyl ($HOCH_2C^\bullet HOH$)	−220.08[11]	12.55	−228.30	8.22	−226.76	6.68
1-ethoxy methyl ($^\bullet CH_2OCH_2CH_3$)	−44.35[11]	12.55	−45.58	1.23	−45.58	1.23
$CH_3O(CO^\bullet)$	−166.94[11]	12.55	−168.91	1.97	−168.91	1.97
$(CH_3)_2C^\bullet OH$	−111.21[10]	4.60	−115.98	4.77		
$CH_3-CH_2-O-C^\bullet H-CH_3$	−84.45[10]	- - -	−92.89	8.44	−91.36	6.91
$^\bullet CH_2COCH_3$	−50.21[11]	6.28	−33.34	16.87		
	−23.88[10]	10.89	−33.34	9.46		
average		4.38		5.47		4.69

[a] Δ = absolute value (mean expt $\Delta_f H°$ − calcd $\Delta_f H°$).

Table 11. Comparison of Predicted $\Delta_f H°$ for Higher Alkyl Radicals by the Present Work and the Difference Method

	difference method[20]	present work old basis		present work new basis	
	$\Delta_f H°$	$\Delta_f H°$	Δ^a	$\Delta_f H°$	Δ^a
radical	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
1-methyl, propyl	66.86	62.13	4.73	63.36	3.50
1-methyl, butyl	45.56	41.21	4.35	42.44	3.12
1-ethyl, propyl	45.56	36.37	9.19	38.83	6.73
2-methyl, butyl	48.79	48.53	0.26	48.53	0.26
1,1-dimethyl, propyl	26.61	17.33	9.28	18.56	8.05
1,2 dimethyl, propyl	38.74	33.26	5.48	33.26	5.48
3-methyl, butyl	48.79	46.44	2.35	47.67	1.12
1-methyl, pentyl	25.36	20.29	5.07	21.52	3.84
1-ethyl, butyl	25.36	15.45	9.91	17.91	7.45
2-methyl, pentyl	27.70	27.61	0.09	27.61	0.09
1,3-dimethyl, butyl	17.66	10.25	7.41	11.48	6.18
4-methyl, pentyl	27.70	25.52	2.18	26.75	0.95
3-methyl, pentyl	30.42	28.87	1.55	30.10	0.32
1,2-dimethyl, butyl	20.38	15.69	4.69	15.69	4.69
2-ethyl, butyl	30.42	30.96	0.54	30.96	0.54
2,3-dimethyl, butyl	24.23	20.92	3.31	20.92	3.31
1,2,2-trimethyl, propyl	6.36	9.41	3.05	17.12	10.76
3,3-dimethyl, butyl	16.40	14.23	2.17	15.46	0.94
average			4.20		3.74

[a] Δ = absolute value [calcd $\Delta_f H°$ (difference method) − calcd $\Delta_f H°$ (present work)].

anyway for the latter. It has already been shown that the GA method with the newly evaluated GAVs predicts $\Delta_f H°$ directly for moderately branched alkyl radicals up to about a carbon number of six fairly closely (see the lower part of Table 8). This gives one the confidence that the estimates presented in Table 11 are expected to be reliable.

Prediction of Enthalpies of Formation of Peroxy Radicals. The GAV for the $O-(O^\bullet)(C)$ group (G24) is required for estimating $\Delta_f H°$ of the $RO_2^\bullet$ radicals, ubiquitous in the oxidation reaction mechanisms. The estimation of the GAV was based on the BDE value originally assigned to the ROO−H bond. Benson and Shaw[24] assigned it to be 376.56 $kJ \cdot mol^{-1}$, which was the same as the best available (at that time) BDE value for the HOO−H bond. Benson and co-workers[26,27] revised this value in the light of more recent data as (370.70 ± 2.51) $kJ \cdot mol^{-1}$. It can be shown that, by following a procedure already discussed under the New Methodologies for Evaluation of the Radical GAVs section and using this BDE value, G24 comes out to be 65.81 $kJ \cdot mol^{-1}$ in place of the 75.31 $kJ \cdot mol^{-1}$ originally assigned by Benson and Shaw.[24]

From a more recent compilation of the bond dissociation energy data,[12] it can be seen that for a number of ROO−H compounds with varying R the experimentally measured BDE values vary by 20.9 to 29.3 $kJ \cdot mol^{-1}$. Clearly this will be reflected in the variation in G24 depending on the chosen BDE value. To get a quantitative feel about this variation, we chose six well-cited hydrperoxides (namely, methyl, ethyl, isopropyl, *tert*-butyl, allyl, and benzyl hydroperoxides) for which experimental values for both the BDE for the ROO−H dissociation and the $\Delta_f H°$ for the corresponding $RO_2^\bullet$ radicals have been

Table 12. Evaluation of the GAV for [O(O•)(C)] Using Reported Experimental Data on BDE or $\Delta_f H^\circ$ for a Number of Hydroperoxides

hydroperoxide ROOH	$\Delta_f H^{\circ\, a}$ ROOH kJ·mol^{-1}	BDE ROO−H kJ·mol^{-1}	$\Delta_f H^\circ$ ROO• calcd kJ·mol^{-1}	$\Delta_f H^\circ$ ROO• expt kJ·mol^{-1}	GAV^b [O(O•)(C)] kJ·mol^{-1}	GAV^c [O(O•)(C)] kJ·mol^{-1}
CH_3OOH	−128.87	370.28[48]	23.43		65.27	
Do				9.20[45]		51.04
Do				10.39[10]		52.22
C_2H_5OOH	−162.76	363.17[45]	−17.57		58.16	
Do				−27.20[49]		48.53
Do				−28.03[29]		47.70
$(CH_3)_2CHOOH$	−200.83	356.06[45]	−62.76		51.04	
Do				−65.27[49]		48.53
$(CH_3)_3OOH$	−240.16	355.6[50]	−102.55		50.63	
Do				−101.67[49]		51.46
$CH_2{=}CH{-}CH_2OOH$	−50.54	363.17[45]	94.64		58.16	
Do				88.70[12]		52.22
$C_6H_5CH_2OOH$	−29.12	363.17[45]	116.06		58.16	
Do				114.64[46]		56.73

[a] Calculated by Benson's GA method. [b] Calculated using the values from column 4. [c] Calculated using the values from column 5.

Table 13. Comparison of the Estimated Heat of Reaction with the Experimental Data for the Reaction R• + O_2 → RO_2• for a Number of R• Radicals

	$\Delta_f H^{\circ\, a}$ R•	$\Delta_f H^{\circ\, a}$ ROO•/kJ·mol^{-1}		$\Delta_r H^\circ$ [=$\Delta_f H^\circ$ (ROO•) − $\Delta_f H^\circ$ R•)]/kJ·mol^{-1}		$\Delta_r H^\circ$/kJ·mol^{-1}
radical R•	kJ·mol^{-1}	[O(O•)(C)] = 56.90 kJ·mol^{-1}	[O(O•)(C)] = 51.04 kJ·mol^{-1}	[O(O•)(C)] = 56.90 kJ·mol^{-1}	[O(O•)(C)] = 51.04 kJ·mol^{-1}	expt^b
methyl	146.56	15.06	9.20	−131.50	−137.36	−135.56[29]
ethyl	120.75	−18.83	−24.69	−139.58	−145.44	−147.28[29]
isopropyl	84.55	−56.90	−62.76	−141.45	−147.32	−157.74[29]
tert-butyl	39.75	−96.23	−102.09	−135.98	−141.84	−153.55[29]
allyl	159.24	93.39	87.53	−65.86	−71.71	−76.15[27]

[a] Calculated by Benson's GA method. [b] Experimentally determined.

reported. In applying the standard procedure, we also require the $\Delta_f H^\circ$ values for the respective ROO−H. In view of the nonavailability of the reliable experimental values for the latter in some cases (for three of the six test compounds), we decided to uniformly use values estimated by the Benson GA method (wherever available, experimental data comes to within 4.2 kJ·mol^{-1} of the estimated values). The fourth column of Table 12 lists the calculated $\Delta_f H^\circ$ values for each of the six radicals, and the fifth column holds the corresponding experimental data. It should be noted that experimental data from a number of sources have been assembled wherever available.

It has to be admitted that while for the isopropyl, *tert*-butyl, allyl, and benzyl peroxy radicals the match between the experimental and the predicted values are quite good, for the methyl and the ethyl radicals there are sizable disparities. We then back-calculated G24 based on both the calculated and the experimental $\Delta_f H^\circ$ values in each of the six cases. These calculation results appear in the sixth and the seventh columns of Table 12. The average value of G24 based on the column 6 is 56.90 kJ·mol^{-1} with a standard deviation of 4.98 kJ·mol^{-1}. The corresponding statistics based on column 7 are 51.04 kJ·mol^{-1} and 2.72 kJ·mol^{-1}, respectively. G24 calculated using the direct experimental $\Delta_f H^\circ$ for the RO_2• radicals (column 7) is slightly lower than one back-calculated from the experimental BDE data (column 6). More importantly, the former set is characterized by less variation about the mean.

Finally, since the data on the directly measured values for the enthalpy change $\Delta_r H^\circ$ associated with the reaction R• + O_2 → RO_2• have been reported[27−29] for a number of R• radicals, we could also compare the predicted enthalpy change for the reaction with the measured ones. The prediction was made by taking the difference between the $\Delta_f H^\circ$ values for R• and RO_2• calculated on the uniform basis of Benson's GA method. We did so using both the above two mean values for G24. The results of this comparative study for five radicals are shown in Table 13. Except for the t-Bu radical, the match is quite good, thereby justifying the GAV estimated in this work. The discrepancy may partly be due to the $\Delta_f H^\circ$ value (low) used here for the *tert*-butyl radical itself. Clearly the lower value of G24 gave a closer match with the experimental data (less absolute deviations for each radical and a closer offset from the 45° straight line parity plot). The recommended GAV for the group [O−(O•)(C)], therefore, is 51.04 kJ·mol^{-1} (the figure that appears in Table 7). It may be noted that in the GAV tabulation by Luo[12] the value reported for the group G24 was −18.8 kJ·mol^{-1}, which is identical to that reported in CB92 for the corresponding molecular group, namely, [O−(O)(C)]. This is clearly not the correct value.

Prediction of the Enthalpy Change Associated with Elementary Reaction Steps. The peroxy and alkoxy radicals are important in the context of the kinetic and the mechanistic studies of liquid-phase oxidation reactions,[25] many of which are known to occur through formation of free radicals and short-lived intermediates (like certain hydroperoxides). The decomposition of the latter in a series of elementary reaction steps and termination of the radicals through bimolecular recombination are well-documented (e.g., in the context of cyclohexane oxidation, see refs 3 and 4). In course of thermo-kinetic hazard evaluation by means of calorimetric studies of the exothermic decomposition of peroxides and hydroperoxides, one comes across similar mechanistic pathways.

A useful input toward the construction of a valid reaction network that explains the overall reaction leading up to the observed products is the enthalpy change for an elementary reaction step, which often involves both the molecular and the radical species. With such data, one can quickly estimate the enthalpy change associated with the overall reaction (comprising of a number of elementary steps), which then can be tallied against the observed enthalpy of reaction data, if available. A reaction network, producing end products identified by detailed

Table 14. Enthalpy of Formation of Species Involved in the Proposed Mechanism of the Thermal Decomposition of Di-*tert*-butyl Peroxide[a]

compound/radical	assignments[b]				$\Delta_f H°$/kJ·mol^{-1}
$(CH_3)_3COOC(CH_3)_3$	$C-(C)(H)_3$ {6}	$C-(C)_3(O)$ {2}	$O-(O)(C)$ {2}		-343.92 (-343.09)[b]
CH_3COCH_3	$C-(CO)(H)_3$ {2}	$CO-(C)_2$ {1}			$-216.31(218.53 \pm 0.42)$[b]
$CH_3COCH_2CH_3$	$C-(CO)(H)_3$ {1}	$CO-(C)_2$ {1}	$C-(C)(H)_3$ {1}	$C-(CO)(C)(H)_2$ {1}	-238.07 (-238.57 ± 0.84)[b]
C_2H_6	$C-(C)(H)_3$ {2}				-83.68 (-83.85 ± 0.29)[b]
$(CH_3)_3COH$	$C-(C)(H)_3$ {3}	$C-(C)_3(O)$ {1}	$O-(O)(H)$ {1}		-311.50 (-312.71 ± 0.88)[b]
$(CH_3)_2C(O)CH_2$ (IBO)	$C-(C)(H)_3$ {2}	$C-(C)_3(O)$ {1}	$O-(C)_2$ {1}	$C-(O)(C)(H)_2$ {1}	-130.96[c]
$(CH_3)_3CO^\bullet$	$C-(C)(H)_3$ {3}	$C-(C)_3(O^\bullet)$ {1}			-89.54
$CH_3COC^\bullet H_2$	$C-(CO)(H)_3$ {1}	**$CO-(C)(C^\bullet)$** {1}	**$C^\bullet-(CO)(H)_2$ {1}**		-50.21
$(CH_3)_3COOC(CH_3)_2C^\bullet H_2$	$C-(C)(H)_3$ {5} **$C^\bullet-(C)(H)_2$ {1}**	$C-(C)_3(O)$ {1}	$O-(O)(C)$ {2}	**$C-(C)_2(C^\bullet)(O)$ {1}**	-179.70

[a] GAVs in bold font are the groups evaluated in the present work. Numbers in curly brackets are group frequencies. [b] Experimental data, taken from NIST Chemistry WebBook.[13] [c] With oxirane correction value.[19]

product analysis, while resulting in a calculated overall enthalpy of reaction close to the observed value (obtained by a calorimetric measurement) as well, will certainly be a good mechanistic candidate for further consideration. In what follows, we demonstrate the calculation of the overall enthalpy change that could take place during the thermal decomposition of di-*tert*-butyl peroxide (DTBP).

The thermal decomposition of DTBP is probably one of the best-studied reactions in chemical kinetics (and is therefore useful for calibrating calorimeters, especially in the temperature range of 120 to 200 °C). Keeping in mind the various early reports on the mechanisms of decomposition of DTBP in the gas phase[30] and in various solvents[31,32] as well as a detailed study of thermal decomposition of cumene hydroperoxide[33] with a very similar product profile as in the case of DTBP, a consistent free radical-based mechanism has been derived[34] and can be presented below:

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3CO^\bullet \qquad \Delta_r H° = 164.85\ \text{kJ·mol}^{-1}$$

$$(CH_3)_3CO^\bullet \rightarrow CH_3COCH_3 + CH_3^\bullet \qquad \Delta_r H° = 19.79\ \text{kJ·mol}^{-1}$$

$$CH_3COCH_3 + CH_3^\bullet \rightarrow CH_3COCH_2^\bullet + CH_4 \qquad \Delta_r H° = -55.31\ \text{kJ·mol}^{-1}$$

$$CH_3COCH_2^\bullet + CH_3^\bullet \rightarrow CH_3COCH_2CH_3 \qquad \Delta_r H° = -334.43\ \text{kJ·mol}^{-1}$$

$$(CH_3)_3COOC(CH_3)_3 + CH_3^\bullet \rightarrow CH_4 + (CH_3)_3COOC(CH_3)_2CH_2^\bullet \qquad \Delta_r H° = -57.20\ \text{kJ·mol}^{-1}$$

$$(CH_3)_3COOC(CH_3)_3 + (CH_3)_3CO^\bullet \rightarrow (CH_3)_3COH + (CH_3)_3COOC(CH_3)_2CH_2^\bullet \qquad \Delta_r H° = -57.74\ \text{kJ·mol}^{-1}$$

$$(CH_3)_3COOC(CH_3)_2CH_2^\bullet \rightarrow (CH_3)_2C(O)CH_2 + (CH_3)_3CO^\bullet \qquad \Delta_r H° = -40.79\ \text{kJ·mol}^{-1}$$

$$2CH_3^\bullet \rightarrow C_2H_6 \qquad \Delta_r H° = -376.81\ \text{kJ·mol}^{-1}$$

leading to the following overall reaction:

$$4(CH_3)_3COOC(CH_3)_3 \rightarrow 4CH_3COCH_3 + (CH_3)_3COH + 2(CH_3)_2C(O)CH_2 + CH_3COCH_2CH_3 + 2CH_4 + C_2H_6 \qquad \Delta_r H° = -133.60\ \text{kJ·mol}^{-1}\ \text{DTBP}$$

For calculating the enthalpy change for each reaction step given above, we first need to calculate the enthalpy of formation of radicals as well as molecules involved in the mechanism. From the last column of Table 14, one can see that except for a few well-known molecules experimental $\Delta_f H°$ data are not available for certain molecular and none of the radical species involved in the proposed mechanism. The GA method with the help of the newly updated radical group values can be used to estimate these quantities. The estimates for the molecular species (Table 14) are quite close to the experimental data. Having successfully demonstrated the ability to do the same for a large number of radicals in the earlier part of this section, estimates of all the pertinent $\Delta_f H°$ values were made with confidence. As seen from this table, we were required to use not only the standard groups tabulated in CB92 but also a few new groups evaluated in this work as well.

Using these data, the enthalpy change ($\Delta_r H°$) for each elementary step as shown above were calculated. These values are shown along with each step in the above reaction network. Some of these calculated values indicate expected[24,25] endothermicity (as for the initiating RO−OR bond rupture) and exothermicity (as for the radical recombination steps). It is instructive to note that several of the intermediate steps appear to be fairly exothermic, and this has an implication for the gross exothermicity (resulting adiabatic temperature rise) of the overall reaction as conducted, say, in an adiabatic calorimeter.

The summation of the enthalpy change for each reaction step (multiplied with a scalar quantity, as required, to balance the overall reaction) is equal to the enthalpy change that can be associated with the overall reaction shown above. The latter is a stoichiometrically balanced equation wherein no radicals appear, and the presence of all the product molecules (gaseous or liquid) appearing on the right-hand side have been verified through the use of appropriate analytical techniques.[35] It must be remembered that the above estimate (-133.60 kJ·mol^{-1}) of the overall $\Delta_r H°$ refers to all species as ideal gas at 25 °C. Accounting for the heat of vaporization of the liquid species (both the reactant DTBP and the products), the overall heat of reaction comes out as -160.7 kJ·mol^{-1}. The reported value of the same quantity is in the range of 151 to 188 kJ·mol^{-1}.[35,36]

Conclusions

In this work we have shown that the estimates of enthalpy of formation of a fairly large number of alkyl- and oxygen-containing radicals that we obtained by the Benson GA method are reliable and within the usual experimental error limit. This has become possible because of our being able to devise simple methodologies to evaluate the GAVs pertinent to these radicals.

For this evaluation, we have used experimental data on the radical enthalpy of formation and bond dissociation energy reported in the literature. The new GAVs for 25 oxygen-containing groups (three of them not reported earlier, 15 of them estimated independently that should replace the earlier assignments) are listed in the Tables 6 and 7. We have also re-evaluated GAVs for the seven existing groups belonging to the alkyl radicals (see Table 3). Though using either of the two approaches for the oxygen-containing radicals gave comparable results, we recommend approach 1 being based on a consistent and new strategy. Similarly, for the alkyl radicals we would recommend the GAVs obtained with the old basis radicals as this procedure gave slightly better results and also reflects the new strategy. This does not mean that the values obtained by the other approach (approach 2) or by using new basis radicals should be rejected. Use of these alternative procedures is valid. Only a self-consistent set of GAVs should be used in a given application, and values from different sets should not be used interchangeably. It is to be hoped that similar methodologies would be extended to other radicals. Finally, we used some of these newly evaluated groups to make reasonably good estimates of the enthalpy change associated with the typical elementary reaction steps in a model peroxide decomposition reaction much cited in the literature.

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