First Principles Based Group Additive Values for the Gas Phase Standard Entropy and Heat Capacity of Hydrocarbons and Hydrocarbon Radicals

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Received: August 21, 2008; Revised Manuscript Received: September 23, 2008

In this work a complete and consistent set of 95 Benson group additive values (GAVs) for standard entropies $S°$ and heat capacities $C_p°$ of hydrocarbons and hydrocarbon radicals is presented. These GAVs include 46 groups, among which 25 radical groups, which, to the best of our knowledge, have not been reported before. The GAVs have been determined from a set of B3LYP/6-311G(d,p) ideal gas statistical thermodynamics values for 265 species, consistently with previously reported GAVs for standard enthalpies of formation. One-dimensional hindered rotor corrections for all internal rotations are included. The computational methodology has been compared to experimental entropies (298 K) for 39 species, with a mean absolute deviation (MAD) between experiment and calculation of 1.2 J mol^{-1} K^{-1}, and to 46 experimental heat capacities (298 K) with a resulting MAD = 1.8 J mol^{-1} K^{-1}. The constructed database allowed evaluation of corrections on $S°$ and $C_p°$ for non-nearest-neighbor effects, which have not been determined previously. The group additive model predicts the $S°$ and $C_p°$ within ~5 J mol^{-1} K^{-1} of the ab initio values for 11 of the 14 molecules of the test set, corresponding to an acceptable maximal deviation of a factor of 1.6 on the equilibrium coefficient. The obtained GAVs can be applied for the prediction of $S°$ and $C_p°$ for a wide range of hydrocarbons and hydrocarbon radicals. The constructed database also allowed determination of a large set of hydrogen bond increments, which can be useful for the prediction of radical thermochemistry.

1. Introduction

Robust modeling of chemical reactors based on radical chemistry requires detailed networks of elementary reactions,[1−4] involving species for which often no accurate thermochemistry is known. For an accurate description of the chemistry involved in radical hydrocarbon conversion processes, fast and accurate methods that provide reliable predictions of the thermochemistry are essential. Experimental determination of all the required thermodynamical data is infeasible, and ab initio calculations, despite their increased accuracy, are computationally too demanding for larger compounds. Therefore structure−property relationships, such as the Benson group additivity method, are particularly useful to predict the thermochemistry for these hydrocarbons.[5−7]

In Benson's group additivity method a group is defined as "an atom together with all of its ligands" and is denoted as $X-(A)_i(B)_j(C)_k(D)_l$ with X the central atom surrounded by *i* ligands A, *j* ligands B, etc. Different types of carbon atoms are distinguished: C stands for a single-, C_d for a double-, and C_t for a triple-bound carbon atom, C_b for a carbon atom in a benzene ring, and C° stands for a carbon radical. The Benson method has been successfully applied for standard enthalpies of formation,[5−9] entropies, and heat capacities[5−7] but also for properties such as crystal densities[10] or enthalpies of vaporization.[11] More recently, group additivity has also been used for the prediction of kinetic parameters.[12−17] For some applications modified group additivity schemes have been developed, such as the correction schemes for non-next-nearest-neighbor halogen−halogen interactions,[12,18,19] the extension for polychlorinated bifenyls of Dorofeeva et al.,[20] or the bond-centered group additivity scheme of Yu et al. for polyaromatics, furans, and *o*-arynes.[21,22] Also the generalized additivity model of Hayes[23] is a promising extension of classical group additivity, varying the size of the additive entity according to the needs using a high-dimensional model representation. Recently, Fishtik[24] proposed a methodology to assess the performance of group additivity methods without the need for the determination of group additive values (GAVs) based on so-called GA reactions, i.e., reactions that conserve the number and type of groups. A very recent paper by Walsh[25] illustrates the continuing usefulness of Benson's group additivity method to obtain numerical values of important thermochemical quantities.

Mariott and White[26] have shown that the accuracy of heat capacities predicted by group additivity is similar to those provided by ab initio vibrational frequencies, particularly for hydrocarbons in which no heteroatoms are present. However, the applicability of the Benson method to radicals is, as for most additivity methods, rather restricted due to the limited number of group additive values available. For enthalpies of formation, the number of available GAVs for radicals[27] was limited to 9 GAVs until the determination of an extra 25 GAVs based on high-level CBS-QB3 calculated standard enthalpies of formation.[9] For entropies and heat capacities, the number of available radical GAVs still remains limited to 9.[28]

The aim of this study is (i) to construct a database of accurate entropies and heat capacities for hydrocarbons and hydrocarbon radicals, calculated at the B3LYP/6-311G(d,p) level including hindered rotor corrections for all internal rotations, (ii) to derive

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10.1021/jp807526n CCC: $40.75

a consistent and accurate set of GAVs for the prediction of $S°$ and $C_p°$ for hydrocarbons and hydrocarbon radicals, (iii) to determine a consistent and accurate set of hydrogen bond increments (HBI) for hydrocarbon radicals, and (iv) to improve the modeling of non-next-nearest neighbor interactions (NNI). The computational methodology is consistent with previous work on standard enthalpies of formation,[9] and the results are compared to the experimental entropy of 39 hydrocarbons and the heat capacity of 46 compounds. The group additive and HBI values are validated by comparing predictions with ab initio calculated values. There are 4 newly reported alkene GAVs, 9 alkyne GAVs, 8 aromatic GAVs, 25 radical GAVs, and 15 HBIs. With the exception of monocyclic aromatics, cyclic hydrocarbons and radicals are not included in this study.

2. Methodology

2.1. Computational Method. Entropies and heat capacities have been calculated using ideal gas statistical thermodynamics:

$$S = k_B\left(\ln Q + T\frac{\partial \ln Q}{\partial T}\right) \tag{1}$$

$$C_p = k_B + k_B T\left(2\frac{\partial \ln Q}{\partial T} + T\frac{\partial^2 \ln Q}{\partial T^2}\right) \tag{2}$$

with Q being the canonical partition functions. Written in molecular partition functions q, this yields

$$S = R\left(1 + \ln\left(\frac{q}{N_A}\right) + T\frac{\partial \ln q}{\partial T}\right) = R\left(\ln q + T\frac{\partial \ln q}{\partial T}\right) - R\ln\left(\frac{e}{N_A}\right) \tag{3}$$

$$C_P = R + RT\left(2\frac{\partial \ln q}{\partial T} + T\frac{\partial^2 \ln q}{\partial T^2}\right) \tag{4}$$

The partition functions are calculated using the Gaussian 03 standard procedures, i.e., assuming separability of the translational, rotational, vibrational, and electronic contributions, and using the rigid external rotation and harmonic oscillator (HO) approximation.[29] The partition functions are corrected for the number of optical isomers by multiplication of the single enantiomer partition function with the number of optical isomers. The geometries and harmonic frequencies are determined at the B3LYP/6-311G(d,p) level. The conformation with minimum electronic energy was selected. A harmonic frequency scaling factor of 0.99 was used, consistent with previous work.[9,30]

Hindered rotor corrections are taken into account for all internal rotations present. The internal rotations are automatically identified on the basis of the topology of the molecule. The 1D-HR approach of Vansteenkiste et al.[31−33] has been applied for the hindered rotor corrections, assuming decoupled internal rotations. The potential energy profiles for internal rotation are determined using a relaxed scan at the B3LYP/6-31G(d) level. This scan of the potential energy V as function of the dihedral angle ϕ is expanded in a Fourier series

$$V(\varphi) = \sum_{k=1}^{n}\frac{1}{2}A_k(1 - \cos(k\varphi)) + \sum_{k=1}^{n}B_k\sin(k\varphi) \tag{5}$$

that is used for the calculation of the partition function for internal rotation. The number of sine and cosine expansion coefficients n is taken as 6. In two cases, i.e., for 2,2,4-trimethylpentane and *cis*-2,5,5-trimethylhex-3-en-2-yl, 9 coefficients were taken as 6 sines and cosines were insufficient to describe the potential energy surface accurately. In the applied method, as described by Vansteenkiste,[31−33] the resulting rotational partition function replaces the harmonic contribution that is derived from the same potential energy profile as determined from eq 5.

For rotational modes with barriers to internal rotation below 1 kJ mol^{-1}, the energy profile for internal rotation was often scattered or discontinuous. Therefore, for these rotations, the free rotor approximation was used for the determination of the partition function for internal rotation:

$$q_{\text{rot.,int}} = \frac{(8\pi^3 I_{m,\text{red.}} k_B T)^{\frac{1}{2}}}{h\sigma} \tag{6}$$

This free rotor contribution replaces the vibrational contribution from the harmonic frequency analysis.

2.2. Estimation of Group Additive Values. Benson groups are local entities that cannot account for nonlocal effects. As entropy contains contributions from molecular symmetry and optical isomerism, which are nonlocal and cannot be modeled by means of group additivity, the intrinsic symmetry-independent entropy S_{int} has to be calculated prior to the estimation of GAVs:

$$S_{\text{int}} = S + R\ln\left(\frac{\sigma}{n_{\text{opt}}}\right) \tag{7}$$

with σ the global symmetry number, i.e., the product of the external symmetry number σ_{ext} and the internal symmetry numbers σ_{int}:

$$\sigma = \left(\prod_k \sigma_{\text{int},k}\right)\sigma_{\text{ext}} \tag{8}$$

Next, the group additive values and corrections for NNI are determined simultaneously by unweighed least-squares analysis, minimizing the following objective function, in which y_i is the ab initio calculated intrinsic entropy $S°_{\text{int}}$ or heat capacity $C_p°$ of molecule i and $\hat{y}_i$ is the group additively calculated value:

$$\text{SSQ} = \sum_{i}^{n}(y_i - \hat{y}_i)^2 \tag{9}$$

This results in the usual equations

$$\overline{\text{GAV}} = (\mathbf{X}^{\mathbf{T}}\mathbf{X})^{-1}\mathbf{X}^{\mathbf{T}}y \tag{10}$$

in which $\overline{\text{GAV}}$ is the estimation vector of group additive values and $\mathbf{X}$ the matrix in which the elements X_{ij} specify the number of occurrences of group j in molecule i. Each of the columns of the matrix of independent variables $\mathbf{X}$ corresponds to a group, and each row corresponds to a molecule. Due to the group definition, each group contains information about the neighboring groups, and therefore the columns in $\mathbf{X}$ are linearly dependent for each class of molecules except for alkanes. Therefore, with the exception of alkanes, the $\mathbf{X}^{\mathbf{T}}\mathbf{X}$ matrix is singular, and there are multiple solutions for the $\overline{\text{GAV}}$ vector. To prevent the linear dependence in the occurrence of some groups, a value has to be assigned to some GAVs. E.g., the alkene $C-(C_d)(H)_3$ group forms a linearly dependent subset with, among others, the $C_d-(C)(H)$ and $C_d-(C)_2$ groups, and therefore the GAV of the $C-(C_d)(H)_3$ group is assigned the value of the $C-(C)(H)_3$ GAV for alkanes. The same procedure was used previously in determining GAVs for standard enthalpies of formation.[9]

The reported significance F of the regression is calculated as

$$F = \frac{\sum_{i=1}^{n} \hat{y}_i^2 / p}{\sum_{i=1}^{n} (\hat{y}_i - y_i)^2 / (n-p)} \tag{11}$$

with n the number of molecules and p the number of estimated GAVs.

Group additive predictions for resonance-stabilized radicals are problematic. However, for entropies and heat capacities resonance effects are much smaller than for standard enthalpies of formation. An unambiguous group additive prediction is only possible for radicals in which the ligands of the radical-centered group include information about all unsaturated bonds that are involved in electron delocalization. This is, e.g., possible for the canonical structure C═C−C°−C═C of diallylic radicals as the $C°-(C_d)_2X$ (X = H, C) group includes both double bonds involved in radical delocalization. In accordance with the general rule for the application of Benson group additivity to radicals, the canonical structure yielding the lowest standard enthalpy of formation is adopted. Radicals for which no unambiguous GA prediction is possible, i.e., radicals without a radical-centered group that includes information about all unsaturated bonds that are involved in electron delocalization, are excluded from the set of radicals to determine GAVs to avoid bias on the GAVs. The omitted species involve radicals with 3 and more conjugated π bonds, for which the resonance stabilization energy can only partially be accounted for using group additivity.

2.3. Non-nearest-neighbor Interactions. The different types of NNI are summarized in Figure 1. For alkanes, corrections are included for the 1,4 gauche interaction (structure 1) and the 1,5 interaction (structure 2). For alkenes, corrections for different types of alkene cis interactions are included in the evaluation: the interaction between two methyl groups, between a methyl group and an alkyl group (other than methyl), or between two alkylic groups (structure 3), a second cis interaction across the same double bond in the case of a tetrasubstitued alkene (structure 4), and interaction of a methyl substituent with a *tert*-butyl group (structure 5). For alkynes a further distinction of cis interactions is made for the ene−yne cis correction (structure 6). In aromatics, the ortho correction for interaction between substituents in the ortho position is included (structure 7). In radicals, the radical gauche type 1 (RG1, structure 8) and type 2 (RG2, structure 9), introduced by Marsi et al.,[34] were accounted for. For allylic radicals, specific allylic cis interaction corrections have been determined (structure 10).

The assignment of the number of corrections for gauche interactions has been performed according to the procedures described previously for enthalpies of formation.[9] For alkanes, this involves the revised gauche counting scheme as introduced by Cohen and Benson.[35] In this scheme, a correction is taken into account for every gauche interaction present. Only for alkanes with multiple gauche interactions across the same bond, the accuracy is improved by taking more correction terms into account than the number of gauche interactions actually present across that bond. The three configurations concerned and the number of gauche corrections that must be accounted for are given in Table 1.

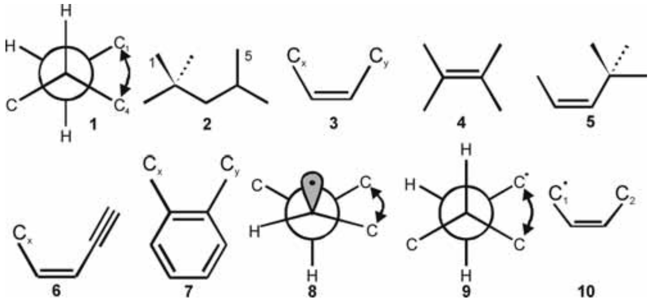
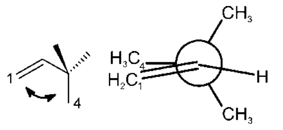
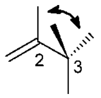


Figure 1. Definitions of non-nearest-neighbor interactions: (1) alkane 1,4-gauche interactions, (2) alkane 1,5-interactions, (3) single cis interaction between C_x and C_y substituents, with *x,y* a methyl or nonmethyl alkyl substituents, (4) double cis interactions, (5) cis interactions with a *tert*-butyl group, (6) ene−yne cis interactions, (7) ortho correction, (8) radical gauche interaction type 1 (RG1) and (9) type 2 (RG2), according to the definition of Marsi et al.,[34] and the radical cis interaction (10).

For alkenes, the same counting procedure for gauche interactions is adopted. However, contributions of non-nearest-neighbor interactions in alkenes can often be accounted for by the GAVs itself, as a C_d ligand necessarily involves bonding to another C_d atom. Possible gauche interactions between the C_d atom bonded to a ligand C_d atom and alkyl substituents on the same group can be accounted for in the GAV of that group.[9] E.g., the group $C-(C_d)(C)_3$ in 3,3-dimethylbut-1-ene, necessarily



involves the interactions between the $C_d-(H)_2$ group of the C_1 carbon atom and the C_4 methyl substituent. These interactions are accounted for implicitly in the GAV of the $C-(C_d)(C)_3$ group and hence should not be accounted for by NNI corrections. Additional gauche interactions that cannot be accounted for implicitly by this group, such as, e.g., the interactions between the methyl substituent on carbon atom 2 and the two methyl substituents on carbon atom 3 of 2,3,3-trimethylbut-1-ene, must still be accounted for explicitly. This results in two



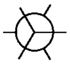
gauche interactions to be accounted for in this molecule. The value of these alkene gauche corrections is taken to be identical to the value of the alkane gauche correction, consistent with the approach used for standard enthalpies of formation.[9]

For alkynes and aromatics the gauche counting approach is similar: all 1,4 interactions are neglected for which the 1,2-bond is a triple bond or part of a benzene ring.

The different types of cis correction in alkenes that are used in literature[5−8,35−37] are summarized in Table 2. It is clear that for cis interactions, the entropy requires a different type of correction than the standard enthalpy of formation. Where for the standard enthalpy of formation the type and number of substituents is crucial, for the entropy the location of the double bond appears to be the important criterion. For heat capacities, no differentiation in the cis correction is found in literature. The nomenclature for entropy cis corrections varies throughout literature and is sometimes inconsistent. Therefore, to avoid confusion the various terms used in literature are provided in the footnotes of Table 2.

For radical gauche interactions in hydrocarbon radicals, introduced by Marsi et al.,[34] the determination of the number

TABLE 1: Number of Gauche Corrections Accounted for in Revised Gauche Counting, for the Cases Where It Differs from Classical Gauche Counting

counting scheme			
classical*	2	4	6
revised	3	5	8

* The number of corrections in classical gauche is equal to the number of interactions that are present.

TABLE 2: Different cis Corrections as Distinguished in Literature

$\Delta_f H°$	$S°$	$C_p°$
single cis	but-2-ene[a]	cis (no distinction)[d]
second cis across the same double bond	3-enes[b]	
cis with one *tert*-butyl structure	other 2-enes[c]	
cis between two *tert*-butyl structures		

[a] Reference: 36, "but-2-ene structure C−C=C−C". [b] Reference: 36, "but-3-ene structure C−C−C=C"; reference: 37, "trienes"; [c] As a zero contribution to the entropy is assumed in previous literature, this correction is usually not tabulated. Sometimes called "other dienes".[37] [d] No differentiation is made.[36] However, for "second cis interaction across the same bond" no correction is applied.[36]

of radical gauche corrections is carried out using the counting scheme proposed in previous work.[9] It provides a counting scheme of radical gauche corrections that is consistent with the revised gauche counting in alkanes and neglect of 1,4-interactions in which the 1,2-bond is a double or triple bond, as in the 3,3-dimethylbut-1-ene example discussed above. According to Marsi et al.[34] a distinction is made between radical gauche type 1, RG1, in which position 2 or 3 of the 1,4-interaction is a radical, and the second type RG2, in which the radical is at position 1 or 4 (see Figure 1, structures 8 and 9). The number of gauche corrections to be accounted for in radicals is determined as follows:

(1) The total number of 1,4-gauche interaction corrections of the type $C_1{-}C_2C_3{-}C_4$, n_{TG}, is determined using revised gauche counting neglecting any radical character. The determination of n_{TG} is based on the rotamer with the minimal number of alkane gauche (AG) interactions as AG interactions are more destabilizing than RG1 and RG2 interactions.

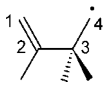
(2) The number of RG1 1,4-interactions, n_{RG1} ($C_1{-}C°_2C_3{-}C_4$; see Figure 1, structure 8) is determined using revised gauche counting and neglecting the radical character of $C°_2$. If one of the central carbon atoms $C°_2$ or C_3 is a C_d, a C_t, or a C_b type of atom, gauche interactions with the adjacent C_d, C_t, or C_b atom can be neglected as these are implicitly taken into account through the GAV of the other central atom.

(3) The number of RG2 1,4-interactions, n_{RG2}, ($C_1°{-}C_2C_3{-}C_4$; see Figure 1, structure 9) is determined using revised gauche counting. If one of the central carbon atoms C_2 or C_3 is a C_d, a C_t, or a C_b type of atom, gauche interactions with the adjacent C_d, C_t, or C_b atom can be neglected as these are implicitly taken into account through the GAV of the other central atom.

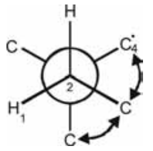
(4) The number of alkane gauche corrections, n_{AG}, to be accounted for in the molecule is then obtained as

$$n_{AG} = n_{TG} - n_{RG1} - n_{RG2} \tag{12}$$

For example, consider the 2,3,3-trimethylbut-1-en-4-yl radical:

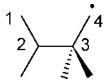


The double bond between positions 1−2 is neglected as the interactions with the group on the C_1 carbon atom can be accounted for in the $C{-}(C°)(C_d)(C)_2$ group. Thus, the 1,4-interactions to be considered are those between groups on a secondary carbon atom (in position 2) and on a quaternary carbon atom (in position 3), i.e., those corresponding with the 3,3-dimethylbut-4-yl radical. Hence, this radical is used for the determination of the number of gauche corrections. For the determination of different number of gauche corrections to be accounted for, the rotamer with the minimum number of AG interactions is considered (numbering consistent with preceding scheme, where the 1−2 double bond has been replaced by a C−H bond as the interactions are accounted for in the $C{-}(C°)(C_d)(C)_2$ group):

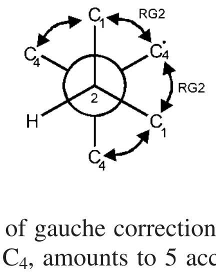


In the first step the total number of gauche corrections, n_{TG}, is determined. The total number of gauche corrections, n_{TG}, for this structure, neglecting the radical character of C_4, is 2 (interactions indicated by arrows). In the second step, the number of RG1 interactions, n_{RG1}, is determined. In this case $n_{RG1} = 0$ as no gauche interactions of the type $C{-}C°C{-}C$ are present in the primary radical. Next, the number of RG2 corrections, n_{RG2}, that can be identified in the above structure is 1. Hence, the number of alkane gauche corrections to be accounted for, $n_{AG} = n_{TG} - n_{RG1} - n_{RG2} = 2 - 0 - 1 = 1$.

As a second example the 2,3,3-trimethylbut-4-yl radical is considered:



The conformation with the maximum number of radical gauche interactions and minimum number of alkane gauche interactions is the rotamer:



The total number of gauche corrections, n_{TG}, neglecting the radical character of C_4, amounts to 5 according to the revised gauche counting scheme (see Table 1, case 2). The number of RG2 interactions, n_{RG2}, that can be identified is 2. Therefore, the number of alkane gauche corrections to be accounted for, n_{AG}, is $5 - 2 = 3$.

2.4. Estimation of Hydrogen Bond Increments. The hydrogen bond increment method assumes that, due the structural similarities between a radical R° and the corresponding parent molecule RH, the entropy and heat capacity of the radical can

TABLE 3: Average Deviations between Ab Initio and Experimental Values for Entropies $S°$(298.15K), Heat Capacities $C_p°$(298K), and Heat Capacities at Higher Temperatures $C_p°$(353−693K) in the Harmonic Oscillator (HO) and 1D-Hindered Rotor (1D-HR) Approximation (Mean Deviation, Mean Absolute Deviation, Root Mean Square Deviation, and Maximum Deviation for the Differences between the Calculated and the Experimental Values from the Sets in *Tables S1−S3* of the *Supporting Information* (J mol^{-1} K^{-1})

	deviations between calculation and experiment					
	$S°$(298K)		$C_p°$(298K)		$C_p°(T)$	
	HO	1D-HR	HO	1D-HR	HO	1D-HR
no. of species	39		46		21	
MD	−4.1	−0.2	−0.4	+0.8	−1.5	−1.2
MAD	5.3	1.2	3.5	1.8	2.8	1.3
rms	7.8	1.6	4.9	2.8	3.7	1.5
MAX	23.0	5.8	15.4	9.1	7.3	3.0

be calculated from that of the parent molecule. The hydrogen bond increments that account for the structural differences between the radical R° and the parent RH are defined as[38]

$$\mathrm{HBI}(S°) = S^{°}_{\mathrm{int,AI}}(\mathrm{R}^{\bullet}) - S^{°}_{\mathrm{int,GA}}(\mathrm{RH}) \tag{13}$$

for the standard entropy and

$$\mathrm{HBI}(C_p^{°}) = C_{p,\mathrm{AI}}^{°}(\mathrm{R}^{\bullet}) - C_{p,\mathrm{GA}}^{°}(\mathrm{RH}) \tag{14}$$

for heat capacities. The subscripts AI and GA denote that $S°$ and $C_p°$ of the radical are calculated directly from the ab initio frequency analysis, while the value for the parent molecule RH is obtained from group additivity using the GAVs determined in this work. Group additive prediction of $S°$ and $C_p°$ for the parent molecule is preferred because in the practical application of the method the value for the parent RH is most likely also calculated using group additivity, as in many cases no experimental or ab initio data are available for the parent molecule.

In the determination of the HBI values for $S°$ and $C_p°$, Lay et al.[38] considered a selected number of vibrational modes. The changes in frequencies of these modes were calculated using generalized frequencies. This differs from this work, in which the HBIs are determined on the basis of full frequency analyses.

3. Results and Discussion

3.1. Experimental Validation. The calculated entropies and heat capacities of the set of 265 species were compared to reference values where possible. The geometries and Fourier expansion coefficients for the energy profiles for internal rotation of all calculated compounds can be found in the Supporting Information.

Entropy. Experimental values were taken from the NIST webbook[39] and from the Computational Chemistry Comparison and Benchmark Database.[40] Most values in the latter are taken from "Thermodynamics of Organic Compounds in the Gas State" by Frenkel et al. published by the Thermodynamics Research Center (TRC),[41,42] and values from the compilation of Gurvich et al.[43]

An overview of the comparison of the calculated values with the experimental values is given in Table 3 for 39 hydrocarbons and hydrocarbon radicals, comprising the results in the harmonic oscillator (HO) and in the 1D-HR approach. These deviations are also graphically represented in Figure 2, showing the fifth, 25th, 75th, and 95th percentiles of the deviations between calculation and experiment. The values for the individual compounds of the set can be found in Table S1 of the Supporting Information. Obviously, the 1D-HR method provides an improvement with the mean absolute deviation (MAD) decreasing from 5.3 to 1.2 J mol^{-1} K^{-1} from HO to 1D-HR approach. The underestimation by the HO approximation is entirely removed in the HR approach, and 95% of the deviations is within 2.8 J mol^{-1} K^{-1} of the reference value. The maximal deviation reduces from 23.0 to 5.8 J mol^{-1} K^{-1}, with the largest remaining deviation of 5.8 J mol^{-1} K^{-1} pertaining to the ethynyl radical, which has no internal rotations. The most significant improvements are observed for alkanes, in which internal rotations are abundant, and alkenes with asymmetric internal rotations such as 1-butene, 1,4-pentadiene, and 2-pentene.

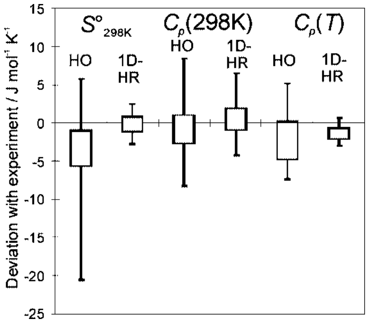


Figure 2. Deviations of $S°$(298K), $C_p°$(298K), and the heat capacity at high temperatures $C_p°(T)$ from experiment. The box shows the 25−75 percentile; the vertical lines give the 5 and 95 percentiles.

A recently published study of Bond[44] reports Gibbs energies calculated using the harmonic oscillator approximation and the term $T\Delta S$ corrected for internal rotation with a fixed value of 1.2 kJ mol^{-1} per rotating bond. For 24 hydrocarbons these results could be compared with ours: in Bond's work the MAD with respect to experiment amounts to 2.7 J mol^{-1} K^{-1} compared to an MAD of 1.3 J mol^{-1} K^{-1} for this work (see Supporting Information Table S2). Overall, the use of a fixed correction per internal rotation, as proposed by Bond, works very well although for individual compounds the entropy can deviate from the experimental value up to 9 J mol^{-1} K^{-1}.

Heat Capacity. The calculated heat capacities $C_p°$ at 298.15 K are compared with values taken from the NIST Webbook,[39] TRC,[41] and Gurvich[43] for 46 hydrocarbons and hydrocarbon radicals. The 1D-HR approach decreases the MAD from 3.5 to 1.8 J mol^{-1} K^{-1} (see Table 3) with 95% of the deviations ranging between −2.1 and 6.6 J mol^{-1} K^{-1} (see Figure 2). The individual deviations are given in Table S3 of the Supporting Information.

The heat capacities are also compared to experiment at higher temperatures because GAVs for $C_p°$ up to 1500 K will be reported. Comparison of the calculated heat capacities with experimental values at higher temperatures requires careful selection of the reference values. Many of the $C_p°$ values reported on the NIST Chemical Webbook pertain to values calculated by correlation schemes, such as from Scott et al.,[45] or statistical thermodynamics functions, such as from TRC.[41] These methods provide accurate values in the temperature range where experimental values are available, commonly the range around 298 K where they have been compared or even fitted to experiment, but the accuracy at higher temperatures is not guaranteed. Therefore, for higher temperatures, only experimental heat capacities were selected. The experimental values reported in Table 3 pertain to the highest temperature available. This temperature differs for every compound, and in the set of 21 species it ranges from 353 to 693 K with an average of 492 K (see Table S4 of the Supporting Information).

TABLE 4: Group Additive Values, Non-nearest Neighbor Interaction Corrections for the $S°$ and $C_p°$ of Alkanes and Regression Statistics for the Estimation, for the Schemes Including and Excluding Corrections for Gauche Interactions (J mol^{-1} K^{-1})

		$C_p°$						
group	$S°$(298K)	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
				Excluding Corrections				
C−(C)(H)$_3$	127.12	25.31	32.07	38.44	44.06	53.36	60.63	72.47
C−(C)$_2$(H)$_2$	39.96	25.05	30.11	35.05	39.40	46.39	51.60	59.63
C−(C)$_3$(H)	−48.97	21.44	27.27	31.71	35.10	39.83	42.89	47.01
C−(C)$_4$	−148.25	17.53	24.47	29.01	31.78	34.22	34.72	33.79
F	1.0×10^5	3.8×10^4	5.3×10^4	7.1×10^4	1.0×10^5	2.4×10^5	5.5×10^5	1.3×10^6
MAD	1.7	1.2	1.1	1.1	1.1	0.8	0.6	0.4
rms	2.3	1.4	1.5	1.5	1.4	1.1	0.8	0.6
MAX	6.1	2.6	2.9	3.5	3.4	2.5	2.1	1.5
				Including Corrections				
C−(C)(H)$_3$	127.20	24.95	31.78	38.21	43.88	53.23	60.51	72.28
C−(C)$_2$(H)$_2$	39.89	25.19	30.21	35.11	39.44	46.42	51.63	59.71
C−(C)$_3$(H)	−48.30	23.31	29.20	33.51	36.70	41.01	43.82	47.82
C−(C)$_4$	−147.80	21.68	28.34	32.40	34.67	36.34	36.51	35.72
1,4-gauche	−0.70	−0.90	−1.08	−1.10	−1.01	−0.76	−0.56	−0.35
1,5-interaction	2.72	−1.42	−0.18	0.55	0.83	0.67	0.18	−0.99
F	1.2×10^5	3.3×10^4	7.6×10^4	1.9×10^5	4.0×10^5	7.8×10^5	8.4×10^5	1.1×10^6
MAD	1.2	0.9	0.7	0.4	0.3	0.3	0.3	0.3
rms	1.6	1.1	0.9	0.7	0.5	0.5	0.5	0.5
MAX	3.5	2.4	2.8	2.3	1.7	1.0	1.4	1.6

From Table 3, it can be seen that at higher temperature, the MAD reduces from 2.8 J mol^{-1} K^{-1} for the HO approximation to 1.3 J mol^{-1} K^{-1} for the 1D-HR approach. The mean deviation however remains −1.2 J mol^{-1} K^{-1} in the 1D-HR approach, mainly caused by some underestimations for alkanes and aromatics. This might be due to neglected anharmonicities for the higher frequencies, which gain in importance at higher temperatures. In Figure 2, the overall improvement of the HR treatment remains clear however.

3.2. Group Additive Values. GAVs have been determined on the basis of calculated entropies $S°$(298.15K) and heat capacities $C_p°(T)$, with T from 300 to 1500 K, for 265 compounds. The calculated entropies and heat capacities are reported in Supporting Information Table S5. The Supporting Information also contains a comparison between the group additive and calculated predictions for all compounds (Table S6).

Alkanes. The Benson method describes alkane thermochemistry using four groups only. According to Benson,[5−7] the group additive predictions of the entropy and heat capacity of alkanes do not require corrections for gauche and 1,5 interactions. Therefore, in a first approach, GAVs were estimated from the set of 16 alkanes without accounting for non-nearest-neighbor interactions; see Table 4. The obtained group additive values compare well to the Benson values, within 1.6 J mol^{-1} K^{-1} for entropies and 2.5 J mol^{-1} K^{-1} for heat capacities (see Table S7 of the Supporting Information). The GAVs determined in this work for the C−(C)(H)$_3$ and the C−(C)$_4$ group are slightly lower than Benson's, while those for the C−(C)$_2$(H)$_2$ and C−(C)$_3$(H) are somewhat higher, both for $S°$ and C_p.

The group additive values for entropy decrease by about 90 J mol^{-1} K^{-1} with each successive substitution of an H ligand by a C ligand, because the entropy contribution of an H atom ligand is fully accounted for in the GAV, while the contribution of a C ligand is described by the group centered on that ligand. E.g., the C−(C)(H)$_3$ group accounts for the contribution of one carbon atom (the central carbon atom) and three hydrogen atoms to the entropy, while the entropy contribution of the C ligand is for the most part accounted for by the group adjacent to this C−(C)(H)$_3$ group. In an atom additive scheme for the entropy of this same set of alkanes, the contribution of an H atom amounts to 91 J mol^{-1} K^{-1}, corresponding very well with the observed difference between the group additive values of about 90 kJ mol^{-1} for each successive substitution.

The difference between the group additively calculated values and the ab initio values for the $S°$ and $C_p°$ of the compounds is smaller than 2 J mol^{-1} K^{-1} for all alkanes except for five compounds (see Table S7 of the Supporting Information). These five species are neopentane, 2-methylpentane, 2,2,3,3-tetramethylbutane, 2,2,4-trimethylpentane, and 2,2,4,4-tetramethylpentane, which are all species with gauche interactions or with groups that are strongly correlated with the presence of gauche interactions. Therefore, in a second approach, 1,4 gauche and 1,5 interaction corrections have been taken into account in the same way as was done for standard enthalpies of formation. The revised gauche counting scheme, introduced by Cohen and Benson, is applied (see section 2.3).[35] As shown previously for the same set of alkanes, the revised gauche counting scheme improves the accuracy of the standard enthalpy of formation compared to the classical gauche counting scheme, particularly for alkanes with multiple gauche interactions across the same bond.[9] The introduction of these NNI corrections for entropies and heat capacities significantly reduces the deviations between group additive predictions and calculated values, except for 2-methylpentane and 2,2,3-trimethylbutane (see Table S7 of the Supporting Information). For these two compounds the deviation between the GA-predicted and AI-calculated $S°_m$ still exceeds 2 J mol^{-1} K^{-1}. Moreover, inclusion of NNI improves the significance of the regression (see Table 4) for the entropy and for the heat capacities at temperatures between 400 and 1000 K. For the heat capacities at 300 and 1500 K a minor decrease in significance is observed.

The value for the 1,4-gauche correction is negative for the entropy and heat capacities at all temperatures. Gauche interactions restrict the internal flexibility in alkanes, resulting in a decrease in entropy and heat capacity. However, the 1,5 interaction correction for the entropy is positive, which is counterintuitive as a 1,5 interaction restricts internal flexibility as well. The reason is most probably due to the fact that species with 1,5 interactions always contain numerous 1,4-interactions. Most likely the 1,5 interaction decreases the effect of the 1,4-

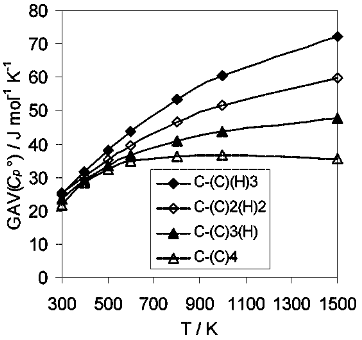


Figure 3. GAVs for the $C_p°$ of alkanes as a function of temperature.

interactions on the internal mobility, resulting in partial compensation of the entropy decrease and hence a positive entropy contribution of the 1,5 interaction correction.

The magnitude of the 1,4 gauche and 1,5 interaction corrections is small, amounting to, respectively, −0.70 and 2.72 J mol^{-1} K^{-1} for entropies and at most to −1.10 and −1.42 J mol^{-1} K^{-1} for heat capacities. However, even in small molecules the 1,4 gauche correction can easily occur 10 times, yielding a total correction for entropies and heat capacities in the order of 10 J mol^{-1} K^{-1}. For standard enthalpies of formation, the corrections for 1,4 gauche and 1,5 interaction are much larger, amounting to respectively 2.9 and 7.1 kJ mol^{-1}, which even at 1000 K influences the Gibbs energy 3−4 times more than the correction on the entropy. However, as the inclusion of the correction improves the significance of the GAV estimates for $S°$ and $C_p°$ and decreases the MAD, the NNI corrections are included in this work.

As the $C_p°$ of alkanes increases with temperature, so increase the GAVs for $C_p°$ with temperature. The temperature dependence of the GAVs is group-dependent, however, as shown in Figure 3. The strongest increase is observed for the $C-(C)(H)_3$ group, and each additional carbon ligand moderates the increase. This trend is largely due to the C−H bonds, which are maximally present in the $C-(C)(H)_3$ group and absent in the most substituted $C-(C)_4$ group. The contribution of the high-frequency C−H stretch modes (3000 cm^{-1}) to the heat capacity GAVs of these groups is only fully developed at about 3400 K, indicating that the GAV will increase with temperature even for temperatures above 1000 K. In contrast, most modes that contribute to the GAV of the more substituted groups as the $C-(C)_4$ group are already fully developed at 1000 K, and the contribution to $C_p°$ will be largely temperature-independent above this temperature.

The temperature dependence of the NNI corrections for $C_p°$ is shown in Figure 4. The magnitude of 1,4 gauche corrections decreases with temperature for $T > 500$ K and remains significantly different from zero except at 1500 K. The temperature behavior of the 1,5 correction is nonmonotonic, and the value evolves roughly from −1 to +1 and back to −1 J mol^{-1} K^{-1}, with a maximum around 600 K. The most probable reason for the observed maximum is that the species with 1,5 interactions have many internal rotations for which the contribution to the heat capacity has a maximum as a function of temperature. Since these internal rotations are typical for a 1,5 interaction, this results in a maximum for the contribution of 1,5 interactions to the heat capacity as a function of temperature. For most internal rotations in compounds without 1,5 interactions, a decrease with temperature of the contribution to $C_p°$ is observed, with only a very feeble maximum at about 400−600 K.

Alkenes. The prediction of entropy and heat capacity for alkenes involves, besides the identification of groups in the molecule, also the determination of the number of gauche interactions (see section 2.3) and the number and type of cis interactions, which are discussed in this section. Group additive values and NNI corrections for alkenes, derived from the entropies or heat capacities of 44 alkenes, are given in Table 5 The comparison of these GAVs with Benson values can be found in Table S9 of the Supporting Information. For six groups no GAVs have been published by Benson, i.e., the $C-(C_d)_2(H)_2$, $C-(C_d)_2(C)(H)$, $C-(C_d)_2(C)_2$, $C-(C_d)_3(H)$, $C-(C_d)_3(C)$, and the $C-(C_d)_4$ groups. For two of these groups, the $C-(C_d)_2(C)(H)$ and $C-(C_d)_3(H)$ groups, Sumathi et al.[46] have provided GAVs on the basis of G2 calculations.

The GAVs compare well with Benson's values, except for the entropy contribution of the $C_d-(C_d)_2$ group, which differs by −12.3 J mol^{-1} K^{-1}, and the heat capacity contribution of the $C-(C_d)(C)_2(H)$ group that differs by +7.53 J mol^{-1} K^{-1} at 300 K.

As for alkanes, each additional hydrogen ligand involves an increase of about 80−110 J mol^{-1} K^{-1} of the GAV, irrespective of the type of the other ligands or the type of the central atom. E.g., the $C_d-(C_d)(H)$ GAV (25.7 J mol^{-1} K^{-1}) is 88.2 J mol^{-1} K^{-1} higher than the GAV of the $C_d-(C_d)(C)$ group.

As mentioned in section 2.3, the contribution of cis interactions to $S°$ and $C_p°$ is mostly related to the location of the double bond, while for the standard enthalpy of formation it is mostly related to the type and number of substituents present on the double bond. The differences in entropies and heat capacities between cis and trans isomers for the individual molecules are given in Table S10 of the Supporting Information. In this work, on the basis of the observed difference between the entropies and heat capacities of cis and trans compounds, five different types of alkene cis corrections to the entropy and heat capacity have been identified (see Table 5): (i) a single cis interaction between two methyl groups, (ii) a single cis interaction between a methyl group and an alkyl group other than methyl, (iii) a single cis interaction between two alkyl groups other than methyl, (iv) a double cis interaction across the same double bond (in this work only calculated from 2,3-dimethyl-2-butene), and (v) a single cis interaction between a methyl and a *tert*-butyl group.

The entropy difference between cis and trans isomers can be positive or negative, depending on the type of substituents on the double bond. The single cis corrections on the entropy range from +5 J mol^{-1} K^{-1} for a methyl−methyl cis interaction to −5 J mol^{-1} K^{-1} for the interaction between two alkyl groups. These single cis contributions to the entropy are mainly caused by a change in the rotational barriers for the internal rotation around the bonds adjacent to the double bond. For the methyl−methyl cis interaction, the cis isomer exhibits a lower barrier for methyl rotation than the trans isomers, which explains the higher entropy for cis isomers. Consider, e.g., but-2-ene in which the barrier to methyl rotation reduces from 8.5 kJ mol^{-1} in the trans isomer to 4.8 kJ mol^{-1} in the cis isomer. As illustrated in Figure 5, the energy difference between cis and trans isomers depends on the coordinate for internal rotation of the methyl substituent. At the rotational minimum of the methyl group, the methyl groups are oriented with one of the C−H bonds of the methyl group in syn position with the C=C bond and the energy difference between cis and trans amounts to 6 kJ mol^{-1}, while at the rotational maximum the energies of cis and trans isomer differ by about 2 kJ mol^{-1} only. At the rotational minimum

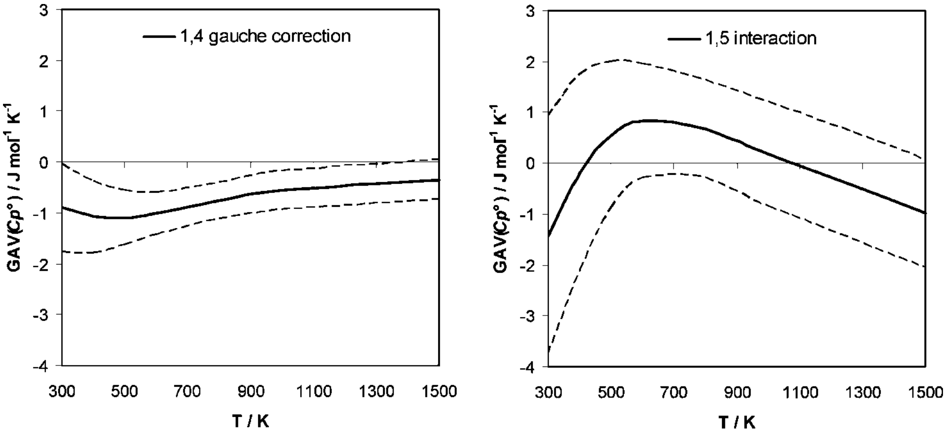


Figure 4. NNI corrections for the $C_p°$ of alkanes as a function of temperature (bold line) and 97.5% confidence intervals (dashed lines).

TABLE 5: Group Additive Values and Non-nearest-Neighbor Interaction Corrections for the $S°$ and $C_p°$ of Alkenes (J mol^{-1} K^{-1})

group	$S°$(298K)	$C_p°$						
		300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
$C-(C_d)(H)_3$	127.20	24.95	31.78	38.21	43.88	53.23	60.51	72.28
$C-(C_d)(C)(H)_2$	41.91	21.93	28.33	33.87	38.47	45.63	50.93	59.18
$C-(C_d)(C)_2(H)$	−49.65	24.94	30.73	35.02	38.03	41.77	44.07	47.41
$C-(C_d)(C)_3$	−142.15	20.74	27.75	32.02	34.38	36.03	36.13	35.39
$C-(C_d)_2(H)_2$	39.93	24.30	30.13	35.27	39.52	46.13	51.10	59.04
$C-(C_d)_2(C)(H)$	−51.11	24.80	31.62	35.72	38.31	41.49	43.59	46.92
$C-(C_d)_2(C)_2$	−144.37	21.40	28.46	32.44	34.57	36.03	36.05	35.17
$C-(C_d)_3(H)$	−47.09	22.35	29.28	33.54	36.30	39.83	42.21	45.98
$C-(C_d)_3(C)$	−157.02	22.88	35.05	40.76	42.57	41.76	39.80	36.50
$C-(C_d)_4$	−160.76	27.84	39.77	45.02	46.17	44.10	41.24	36.90
$C_d-(H)_2$	115.76	20.59	25.93	30.75	34.87	41.44	46.45	54.57
$C_d-(C)(H)$	32.91	18.44	21.74	25.02	27.96	32.65	36.06	41.17
$C_d-(C)_2$	−55.9	19.58	21.71	23.12	24.25	25.94	27.02	28.35
$C_d-(C_d)(H)$	25.73	18.10	24.14	29.11	32.72	37.14	39.66	43.06
$C_d-(C_d)_2$	−49.16	18.68	19.20	18.83	18.80	20.02	21.79	25.04
$C_d-(C_d)(C)$	−62.49	18.57	23.97	26.76	28.02	28.75	28.88	28.97
C_a	25.58	15.24	17.29	18.73	19.79	21.26	22.24	23.53
methyl−methyl cis	5.29	−5.68	−5.48	−4.64	−3.79	−2.57	−1.84	−0.98
methyl−alkyl cis	−1.04	−4.70	−2.80	−1.11	−0.02	0.85	0.94	0.60
alkyl−alkyl cis	−5.02	−4.06	−0.78	1.62	2.95	3.64	3.29	1.96
double cis	13.92	−16.70	−16.10	−13.67	−11.20	−7.61	−5.43	−2.87
methyl−*tert*-butyl cis	2.08	−5.18	−5.27	−5.21	−4.96	−4.16	−3.36	−2.02
significance *F*	7.9×10^3	2.9×10^3	3.5×10^3	5.0×10^3	7.7×10^3	1.8×10^4	4.2×10^4	2.1×10^5
MAD	1.4	1.1	1.1	1.1	1.1	0.8	0.6	0.3
rms	2.2	1.6	1.8	1.8	1.6	1.2	0.9	0.4
MAX	5.9	4.4	4.7	4.3	3.8	2.9	2.1	1.1

of the methyl group, there is an important 1,6 H−C−C═C−C−H steric interaction between the hydrogen atoms of the two cis methyl groups (H−H distance, 212 pm). This interaction decreases as the methyl group rotates away toward its rotational maximum (H−H distance, 268 pm). In the trans isomer, the 1,6 H−C−C═C−C−H is absent, and the 1,5 H−C−C═C−H interaction is much less pronounced with an H−H distance of 243 pm. Hence, the decrease in rotational barrier in going from trans to cis isomer is mainly caused by an upward shift of the minimum in the potential energy profile in the cis isomer due to the presence of the strong 1,6 H−C−C═C−C−H steric interaction. This upward shift of the methyl rotational minimum in the cis isomer is of the same magnitude as the enthalpy difference between trans and cis isomers, which amounts to 3.1 kJ mol^{-1}.[39] The energies of the rotational maxima remain almost the same as with the C−H bond in gauche position to the C═C bond, and there is little additional strain in the cis isomer.

If the methyl groups are replaced by more bulky alkyl groups, the picture is reversed, and now the largest difference between cis and trans energies occurs for the maximum of the internal rotation profile, rather than for the minimum as illustrated in Figure 6 for 3-hexene. In the rotational minimum, the 1,6 H−C−C═C−C−H interaction between the two hydrogen atoms in syn position still increases the energy of the cis isomer, but the energy increase at the rotational maximum due to the substituents is far more pronounced in this case. Therefore, for the alkyl−alkyl cis interaction, the rotational barrier for the internal rotation about the bond adjacent to the C═C double bond is higher in the cis isomer explaining the lower entropy for the cis isomers. The alkyl−alkyl cis interaction is a generalization of Benson's so-called "3-enes" cis interaction.

The methyl−alkyl cis correction describes the interaction between a methyl and an alkyl group other than methyl. The effect on the entropy is therefore a mixture of the two previously discussed types of single cis interaction with an increasing effect of the methyl rotor and a decreasing effect of the alkyl rotor on the entropy of the cis isomer. The value of −1.04 J mol^{-1} K^{-1} for this correction indicates that the decreasing effect due to the alkyl rotation is slightly more pronounced than the increasing

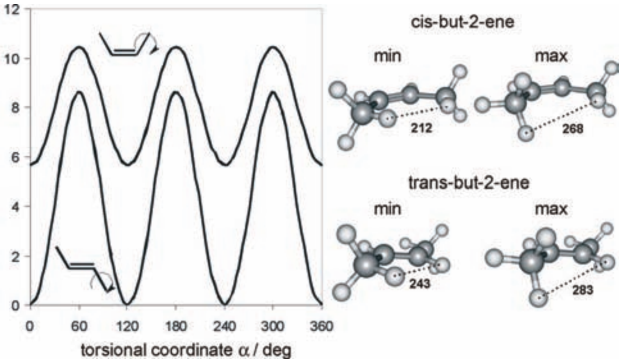


Figure 5. Potential energy profile for the methyl internal rotation in *cis*- (upper) and *trans*-but-2-ene (lower), explaining the higher entropy for the cis isomer. The electronic energy is plotted relative to E_{ref}, the minimum energy of the *trans*-2-butene profile. (distances in pm)

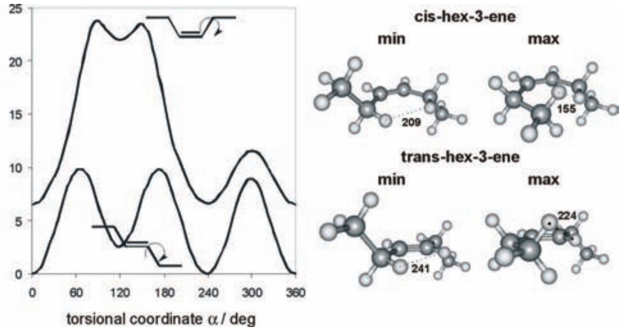


Figure 6. Potential energy profile for the ethyl internal rotation in *cis*- (upper) and *trans*-hex-3-ene (lower), explaining the lower entropy for the cis isomer. The energy is plotted relative to the minimum energy of the *trans*-3-hexene profile. (distances in pm)

effect due to the methyl rotation. This value has been determined from alkenes substituted with secondary and tertiary groups; no quaternary groups such as *tert*-butyl are included as these have a different effect on the heat capacity.

The correction for the double cis interaction (see Figure 1, structure 4) is derived from 2,3-dimethylbut-2-ene and amounts to 13.92 J mol^{-1} K^{-1} for the entropy. This is more than twice the correction for methyl−methyl cis correction, which sums up to 10.58 J mol^{-1} K^{-1}, due to an even lower barrier to methyl rotation (2.5 J mol^{-1} K^{-1}) than for the single methyl−methyl cis interaction (4.8 J mol^{-1} K^{-1} in but-2-ene).

The methyl−*tert*-butyl cis interaction (see Figure 1, structure 5) is essentially a subtype of the interaction between a methyl and an alkyl group. Because of changes on the cis correction for $C_p°$ up to 5 J mol^{-1} K^{-1}, this type of interaction is distinguished from the others. For enthalpies of formation, *tert*-butyl cis interaction constitutes a separate cis correction as well.

Alkynes. Predictions for alkynes involve, next to the previously determined GAVs and NNI corrections, GAVs for 28 alkyne-specific groups and one NNI correction, the ene−yne cis correction (see Figure 1, structure 6). The GAVs for alkynes are summarized in Table 6 and compared to Benson GAVs in Table S11 of the Supporting Information. Only for nine of the 28 groups, GAVs for $S°$ and $C_p°$ have been determined from experiment, and for an additional 10 group ab initio values have been determined by Sumathi et al.[46] The GAVs of the nine groups agree within 2.5 J mol^{-1} K^{-1} with the experimentally determined Benson values for $S°$ and $C_p°$, except for the $C_t-(C_d)$, the $C-(C_t)(C)_2(H)$, and the $C-(C_t)(C)_3$ groups. The deviations on the $C_t-(C_d)$ GAVs for $C_p°$ can be due to a typographical error in Benson's GAVs, as suggested by Sumathi et al.[46] The deviation on the $C-(C_t)(C)_3$ GAV for $C_p°$, up to 20.8 J mol^{-1} K^{-1} for $C_p°$(298K), might also be due to a typographical error in Poling et al.[36] for the $C-(C_t)(C)_3$ GAV. Using the GAVs from Poling et al. for the prediction of the $C_p°$(298K) of 3,3-dimethylbut-1-yne, which contains the $C-(C_t)(C)_3$ group, yields a value that is 18 J mol^{-1} K^{-1} lower than the value determined by TRC[41] on the NIST Webbook[39]. Use of the GAVs determined in this work, however, yields a heat capacity within 0.1 J mol^{-1} K^{-1} of the NIST value.

As for alkanes and alkenes, each additional hydrogen ligand involves an increase of about 80−100 J mol^{-1} K^{-1} of the GAV for $S°$. A second-order effect is observed in the number of C_t ligands: for each subset with a fixed number of H ligands, an increase of 3−7 J mol^{-1} K^{-1} in the GAV is observed for each replacement of a C or C_d ligand by a C_t ligand.

The ene−yne cis correction is, with the largest contribution to $C_p°$ of 1.32 J mol^{-1} K^{-1} at 300 K, not significantly different from zero. The correction is retained, however, to be consistent with the approach for standard enthalpies of formation, where the ene−yne cis contribution is found to be stabilizing by −3.2 kJ mol^{-1}, in contrast to the destabilizing character of the cis interactions between alkyl substituents.

Monocyclic Aromatics. Twenty GAVs for aromatics, from which 8 have never been determined before, are reported in Table 7. These GAVs are in good agreement with the Benson values (Supporting Information Table S12). The apparently large deviation for the entropy contribution of the $C_b-(C_t)$ group, which differs by −10.6 J mol^{-1} K^{-1} from Benson's value, results from the fact that the $C_b-(C_t)$ group always occurs together with the $C_t-(C_b)$ group, for which the GAV is set equal to the GAV of the $C_t-(C_d)$ group. The latter GAV differs by +6.0 J mol^{-1} K^{-1} from the Benson value. Because these $C_b-(C_t)$ and $C_t-(C_b)$ groups always occur together, the sum of the deviations on the GAVs should be accounted for, which only amounts to 4.6 J mol^{-1} K^{-1}. For the heat capacity GAVs of these groups, summing the deviations also reduces the deviations from the Benson GAVs to less than 3 J mol^{-1} K^{-1}.

In addition, ortho corrections for disubstituted aromatics have been determined from methyl- and ethyl-substituted benzenes. Because there is almost no difference in entropy or heat capacity between 1,3- and 1,4-substituted benzenes (at most 0.4 J mol^{-1} K^{-1} on the entropy of methylethylbenzenes), the ortho contributions are calculated from the difference between the 1,2- and 1,3-substituted species. The similarity in magnitude of the ortho corrections for the studied methyl- and ethyl-substituted benzenes allows grouping of all the ortho corrections into a single ortho correction of −5.7 J mol^{-1} K^{-1} for the entropy and 1.1 to 3.2 J mol^{-1} K^{-1} on the heat capacity $C_p°(T)$. The negative value for the ortho correction on the entropy results from the free rotor characteristics of the substituents in the 1,3 and 1,4 positions, while the substituents in the 1,2 position experience mutual steric strain. The free rotors have a higher entropy contribution than the strained rotors, resulting in a negative value for the ortho correction for entropy.

Hydrocarbon Radicals: GA Method. *(a) Group Additive Values.* The thermochemistry of radicals (up to monocyclic aromatic radicals) can be described using 125 groups, in addition to the nonradical groups mentioned in the previous sections. These 125 groups can be divided into 41 radical-centered and 84 radical-adjacent groups, which have a radical carbon atom as a ligand. The estimation of these 125 GAVs and the assessment of the accuracy of the group additivity method would thus require a very large ab initio database of

TABLE 6: Group Additive Values and Non-nearest Neighbor Interaction Corrections for the $S°$ and $C_p°$ of Alkynes (J mol^{-1} K^{-1})

		$C_p°$						
group	$S°$(298K)	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
$C_t-(H)$	102.94	21.61	24.75	26.96	28.65	31.28	33.41	37.21
$C_t-(C)$	26.45	13.78	15.34	16.73	17.93	19.82	21.15	22.98
$C_t-(C_d)$	32.95	11.77	12.63	13.12	13.85	15.83	17.80	21.00
$C_t-(C_t)$	23.79	14.32	16.62	18.08	19.15	20.68	21.73	23.21
$C-(C_t)(H)_3$	127.20	24.95	31.78	38.21	43.88	53.23	60.51	72.28
$C-(C_t)(C)(H)_2$	42.72	20.94	27.92	33.77	38.53	45.76	51.05	59.24
$C-(C_t)(C)_2(H)$	−45.65	20.06	26.82	31.74	35.25	39.80	42.68	46.75
$C-(C_t)(C)_3$	−138.09	21.15	27.97	31.92	34.02	35.44	35.52	34.87
$C-(C_t)(C_d)(H)_2$	41.75	19.36	27.31	33.54	38.39	45.60	50.84	58.98
$C-(C_t)(C_d)(C)(H)$	−44.84	19.96	26.93	31.76	35.09	39.38	42.16	46.22
$C-(C_t)(C_d)(C)_2$	−140.89	24.09	30.13	33.26	34.72	35.41	35.19	34.38
$C-(C_t)(C_d)_2(H)$	−50.17	24.86	30.48	34.20	36.71	40.04	42.37	46.04
$C-(C_t)(C_d)_2(C)$	−139.15	19.89	27.44	31.24	32.98	33.95	33.95	33.50
$C-(C_t)(C_d)_3$	−144.38	22.07	30.12	33.77	35.13	35.35	34.84	33.76
$C-(C_t)_2(H)_2$	45.77	18.35	26.25	32.52	37.49	44.96	50.40	58.80
$C-(C_t)_2(C)(H)$	−42.13	17.44	25.10	30.40	34.10	38.85	41.87	46.15
$C-(C_t)_2(C)_2$	−134.34	18.60	26.09	30.31	32.54	34.17	34.42	34.08
$C-(C_t)_2(C_d)(H)$	−40.35	16.07	24.55	30.02	33.65	38.26	41.25	45.60
$C-(C_t)_2(C_d)(C)$	−135.79	19.21	26.74	30.64	32.52	33.71	33.81	33.48
$C-(C_t)_2(C_d)_2$	−141.31	25.63	31.76	34.16	34.83	34.59	34.05	33.23
$C-(C_t)_3(H)$	−37.85	15.08	23.29	28.72	32.47	37.43	40.70	45.41
$C-(C_t)_3(C)$	−129.64	16.43	24.38	28.66	30.93	32.74	33.21	33.28
$C-(C_t)_3(C_d)$	−129.97	15.47	24.24	28.50	30.49	31.92	32.31	32.50
$C-(C_t)_4$	−123.62	14.83	22.85	26.85	28.90	30.72	31.47	32.16
$C_d-(C_t)(H)$	25.73	18.10	24.14	29.11	32.72	37.14	39.66	43.06
$C_d-(C_t)(C)$	−58.15	16.79	21.34	24.70	26.89	28.95	29.56	29.64
$C_d-(C_t)(C_d)$	−60.65	12.34	16.43	18.86	20.72	23.78	26.11	29.41
$C_d-(C_t)_2$	−64.78	16.30	23.53	28.58	31.49	33.40	33.19	31.63
ene−yne cis	0.87	−1.32	−0.51	−0.04	0.18	0.28	0.23	0.10

TABLE 7: Group Additive Values for the $S°$ and $C_p°$ of Aromatics (J mol^{-1} K^{-1})

		$C_p°$						
group	$S°$(298K)	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
$C_b-(H)$	48.22	13.62	18.63	22.9	26.35	31.41	34.92	40.12
$C_b-(C)$	−33.23	10.30	13.56	16.42	18.77	22.05	24.04	26.38
$C_b-(C_d)$	−31.53	12.15	14.72	16.64	18.34	21.19	23.24	25.93
$C_b-(C_t)$	−43.24	14.11	19.14	22.89	25.34	27.71	28.45	28.68
$C-(C_b)(H)_3$	127.20	24.95	31.78	38.21	43.88	53.23	60.51	72.28
$C-(C_b)(C)(H)_2$	39.50	24.73	30.33	35.46	39.81	46.59	51.64	59.55
$C-(C_b)(C)_2(H)$	−51.95	24.68	30.18	34.20	37.10	40.95	43.47	47.15
$C-(C_b)(C)_3$	−144.10	22.70	28.58	31.96	33.75	34.96	35.04	34.54
$C-(C_b)(C_d)(H)_2$	39.40	23.74	30.65	36.11	40.40	46.89	51.72	59.39
$C-(C_b)(C_d)(C)(H)$	−46.68	21.06	27.35	31.90	35.10	39.22	41.76	45.00
$C-(C_b)(C_d)_2(H)$	−51.14	22.01	28.52	32.94	35.90	39.69	42.21	46.02
$C-(C_b)(C_t)(H)_2$	40.40	19.32	26.77	32.83	37.70	45.09	50.48	58.82
$C-(C_b)(C_t)(C)(H)$	−48.86	23.48	29.38	33.50	36.41	40.28	42.81	46.59
$C-(C_b)(C_t)(C)_2$	−143.56	22.69	28.82	32.13	33.78	34.77	34.71	34.14
$C-(C_b)(C_t)(C_d)(H)$	−41.08	21.55	28.56	33.03	35.93	39.43	41.53	44.34
$C_d-(C_b)(H)$	25.73	18.10	24.14	29.11	32.72	37.14	39.66	43.06
$C_d-(C_b)(C)$	−59.73	16.35	20.32	23.19	25.12	27.09	27.83	28.13
$C_d-(C_b)(C_d)$	−75.23	23.23	28.96	31.20	31.85	31.56	30.76	28.87
$C_d-(C_b)(C_t)$	−67.01	15.85	22.79	27.61	30.34	32.10	31.77	29.80
$C_t-(C_b)$	32.95	11.77	12.63	13.12	13.85	15.83	17.80	21.00
ortho correction	−5.73	3.23	2.36	1.97	1.79	1.65	1.53	1.08

entropies and heat capacities. For standard enthalpies of formation $\Delta_f H°$, the required number of 125 GAVs could be reduced to 41 without a great loss of accuracy, by setting the GAVs of the 84 radical-adjacent groups equal to the GAVs of the corresponding nonradical hydrocarbon groups.[9] The corresponding nonradical hydrocarbon group is obtained by replacing the radical carbon atom by its nonradical equivalent; e.g., $C_d-(C)_2(H)_2$ is the corresponding hydrocarbon group of $C_d-(C°)(C)(H)_2$. Therefore, the need to include the radical-adjacent GAVs in the GA method for radical entropies and heat capacities has been assessed.

In the set of 131 studied radicals, 34 radical and 22 radical-adjacent groups occur. If the GAVs of these 22 radical-adjacent groups are not estimated but set equal to the value of the corresponding nonradical hydrocarbon groups, the significance of the regression remains the same for entropies and reduces slightly for heat capacities (see Table 8). Also, the very small increase (≤0.5 J mol^{-1} K^{-1}) of the MAD between the GA predicted and the ab initio calculated entropies and heat capacities is acceptable. For the individual radicals, the changes in entropy and heat capacity remain limited to 3 J mol^{-1} K^{-1} for 124 out of the 131 species (see

TABLE 8: Regression Statistics for the Estimation of Radical GAVs (Significance F, Mean Absolute Deviation, Root Mean Square Deviation, and Maximum Deviation (J mol^{-1} K^{-1}))

		C_p°						
	S°(298K)	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
Estimation of Radical and Radical-Adjacent Groups (Excluding RG1 and RG2)								
F	3.9×10^3	8.4×10^2	1.6×10^3	2.6×10^3	3.9×10^3	8.3×10^3	1.6×10^4	5.2×10^4
MAD	1.3	1.0	0.9	0.8	0.7	0.6	0.4	0.3
rms	2.1	1.5	1.3	1.2	1.1	0.9	0.7	0.4
MAX	6.4	7.1	6.0	5.2	5.0	4.1	3.2	1.9
Estimation of Radical Groups, Taking a Nonradical Equivalent of Radical-Adjacent Groups (Excluding RG1 and RG2)								
F	3.5×10^3	2.2×10^2	5.7×10^2	1.0×10^3	1.6×10^3	3.3×10^3	6.4×10^3	2.0×10^4
MAD	1.7	1.5	1.1	1.0	0.9	0.6	0.5	0.3
rms	2.6	2.2	1.6	1.4	1.2	1.0	0.8	0.5
MAX	7.7	8.8	5.6	5.0	4.9	4.2	3.3	2.2
Estimation of Radical Groups, Taking Nonradical Equivalent of Radical-Adjacent Groups (Including RG1 and RG2)								
F	3.4×10^3	2.2×10^2	6.9×10^2	1.5×10^3	2.5×10^3	5.2×10^3	9.7×10^3	3.0×10^4
MAD	1.7	1.4	1.0	0.8	0.7	0.5	0.4	0.3
rms	2.5	2.0	1.4	1.1	0.9	0.7	0.6	0.4
MAX	7.5	8.8	5.2	3.2	3.0	3.0	2.5	1.5

Table S13 of the Supporting Information). Therefore, in line with the approach for standard enthalpies of formation $\Delta_f H^\circ$, the GAVs of all radical-adjacent groups can be set equal to the GAVs of the corresponding hydrocarbon groups without much loss of accuracy.

The obtained GAVs for S° and C_p° of the radical groups are reported in Table 9. The GAVs of the radical-adjacent groups can be found in the previous tables, as these are taken equal to the corresponding hydrocarbon equivalents. From the 34 reported GAVs, 25 have not been determined before. For the nine GAVs that had already been determined by O'Neal and Benson in 1973,[28] there are large differences with the GAVs reported in this work. Particularly for entropies the GAV differ up to 22 J mol^{-1} K^{-1}. The differences with the more recently determined GAVs reported by Cohen[27] are limited to 6 J mol^{-1} K^{-1}.

(b) NNI. Two types of NNI interactions specific to radicals are studied: first, radical gauche interactions, and second, radical-specific cis interactions.

Gauche interactions in radicals are modeled using the radical gauche 1 and radical gauche 2 (RG1 and RG2) corrections introduced by Marsi et al. for the standard enthalpy of formation (see Figure 1, structures 8 and 9).[34] The counting scheme for these radical gauche corrections, as introduced in previous work,[9] has been discussed above (section 2.3). To our knowledge, the need to include these radical gauche corrections for the group additive prediction for entropy and heat capacity has not been assessed before.

Our results point out that refinement of the gauche interactions into (revised) alkane gauche, RG1 and RG2, offers significant improvement for larger species with many gauche interactions, such as tri- and tetramethyl-substituted butyl and pentyl radicals. This has been verified by estimating two sets of GAVs: a first set, in which all 1,4 interactions are treated as alkane gauche corrections, and a second estimation, in which the gauche correction was divided into corrections for alkane gauche, radical gauche RG1 and RG2. For both estimations the differences between GA prediction and ab initio value were calculated. The species for which the difference between the two approaches exceeds 1 J mol^{-1} K^{-1} on S°(298K) or C_p°(300K) are tabulated in Table S14 of the Supporting Information. For entropy, the largest improvement due to the inclusion of RG1 and RG2 corrections is 3.2 J mol^{-1} K^{-1} for the *tert*-butyl radical, in which no alkane gauche interactions are present but in which the central $C^\circ-(C)_3$ group is strongly correlated with the presence of radical gauche interactions. For heat capacity the largest improvement is 2.4 J mol^{-1} K^{-1} for the 2,4,4-trimethyl-2-pentyl radical. Of course, these individual improvements only slightly decrease the overall MAD between the GA prediction and the ab initio calculation (see Table 8), as these radical gauche interactions appear only in 26 of the 131 radicals in the set.

The magnitude of the radical gauche corrections is small, +0.8 and −0.9 J mol^{-1} K^{-1} for the RG1 and RG2 contribution to the entropy and at most −1.0 and +0.6 J mol^{-1} K^{-1}, respectively, for the heat capacities. However, the corrections on C_p° are significantly different from zero for temperatures above 500 K (see Figure 7). The effect of radical gauche corrections for S° and C_p° is smaller than for standard enthalpies of formation, but the corrections provide a substantial improvement for strongly substituted radicals requiring easily up to 10 corrections.

The cis interactions in allylic radicals are a second type of radical-specific interactions that require corrections. These allylic cis interactions ($C_1^\circ-C{=}C-C_2$), see Table 10, are structurally different from cis interactions in alkenes ($C-C{=}C-C$) due to the radical character of one of the interacting groups. Therefore, the contributions to the entropy and heat capacity of these allylic cis interactions are evaluated. The allylic cis contributions are calculated from the difference in entropy between the trans and cis isomer. The results are reported in Table 10 for varying substituents on the C_1 allylic carbon atom and the C_2 carbon.

For the entropy, the allylic cis corrections vary between −13.3 and +2.7 J mol^{-1} K^{-1}. In general, there is a positive entropy contribution at low substitution levels of C1 and C2 and a negative entropy contribution at higher substitutions, in parallel with the results obtained for cis interaction in alkenes. Exception is the bulky *tert*-butylic substituent $C_2-(C_d)(C)_3$, for which an entropy increase occurs at low C_1 substitution. For the cis

TABLE 9: Group Additive Values and Non-nearest-Neighbor Interaction Corrections for the $S°$ and $C_p°$ of Radicals, with the Radical-Adjacent GAVs Set Equal to the GAV of the Corresponding Nonradical Groups (J mol^{-1} K^{-1})

		$C_p°$						
group	$S°$(298K)	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
$C°-(C)(H)_2$	139.01	22.79	27.81	32.10	35.67	41.33	45.76	53.10
$C°-(C)_2(H)$	56.57	18.53	21.25	24.24	26.99	31.44	34.71	39.53
$C°-(C)_3$	−22.82	11.49	13.96	16.76	19.19	22.54	24.46	26.39
$C°-(C_d)(H)_2$	117.96	21.40	28.87	34.63	38.99	45.28	49.87	57.25
$C°-(C_d)(C)(H)$	35.99	18.28	23.44	27.72	31.02	35.66	38.81	43.43
$C°-(C_d)(C)_2$	−46.53	13.09	16.90	20.15	22.68	25.96	27.80	29.76
$C°-(C_d)_2(H)$	16.49	17.36	25.75	31.54	35.44	40.27	43.29	47.62
$C°-(C_d)_2(C)$	−71.99	12.47	21.07	26.66	30.09	33.32	34.48	35.06
$C°-(C_d)_3$	−79.68	13.98	23.08	28.62	31.85	34.95	36.29	37.56
$C°-(C_t)(H)_2$	130.78	26.91	31.65	35.48	38.63	43.64	47.55	54.15
$C°-(C_t)(C)(H)$	56.06	17.17	22.25	26.02	28.88	32.91	35.66	39.70
$C°-(C_t)(C)_2$	−27.36	14.14	16.78	19.08	20.96	23.49	24.90	26.33
$C°-(C_t)(C_d)(H)$	32.79	18.21	25.25	29.99	33.24	37.38	40.04	43.97
$C°-(C_t)(C_d)(C)$	−48.31	13.48	19.08	22.69	25.03	27.59	28.82	30.01
$C°-(C_t)(C_d)_2$	−69.50	13.67	21.94	26.74	29.47	32.04	33.09	34.01
$C°-(C_t)_2(H)$	49.06	19.04	24.63	28.28	30.87	34.40	36.78	40.39
$C°-(C_t)_2(C)$	−29.99	13.33	17.69	20.40	22.22	24.34	25.37	26.35
$C°-(C_t)_3$	−34.14	14.57	20.03	22.79	24.33	25.81	26.35	26.72
$C°-(C_b)(H)_2$	112.64	27.98	34.37	38.93	42.31	47.39	51.30	57.91
$C°-(C_b)(C)(H)$	32.41	19.97	25.68	29.93	33.06	37.38	40.25	44.35
$C°-(C_b)(C)_2$	−51.18	15.48	19.01	21.83	23.96	26.78	28.37	30.02
$C°-(C_b)(C_d)(H)$	15.05	22.25	29.21	33.96	37.15	41.26	43.92	47.87
$C°-(C_b)(C_d)(C)$	−71.77	17.88	23.34	26.89	29.12	31.55	32.72	33.89
$C°-(C_b)(C_d)_2$	−87.13	18.62	26.49	31.16	33.79	36.26	37.26	38.09
$C°-(C_b)(C_t)(H)$	29.88	22.97	28.65	32.39	34.95	38.41	40.74	44.31
$C°-(C_b)(C_t)(C)$	−53.12	20.43	23.78	25.92	27.32	28.96	29.75	30.46
$C°-(C_b)(C_t)(C_d)$	−67.31	19.25	25.74	29.36	31.33	33.12	33.78	34.29
$C_d°-(H)$	121.36	20.59	23.57	25.74	27.44	30.14	32.31	35.96
$C_d°-(C)$	41.33	16.74	17.40	18.26	19.11	20.49	21.39	22.40
$C_d°-(C_d)$	37.49	16.93	17.91	18.53	19.28	21.01	22.54	24.73
$C_d°-(C_t)$	43.98	24.57	25.82	26.77	27.22	27.17	26.56	25.14
$C_d°-(C_b)$	27.88	21.56	24.51	26.32	27.25	27.88	27.88	27.50
$C_t°-$	112.58	21.44	19.65	18.53	17.95	17.63	17.71	18.08
$C_b°-$	53.18	12.13	14.69	16.57	17.87	19.51	20.41	21.33
RG1	0.82	−0.93	−0.73	−0.70	−0.71	−0.69	−0.63	−0.47
RG2	−0.87	0.53	0.59	0.61	0.59	0.49	0.38	0.25

isomer, the *tert*-butylic internal rotor associated with the $C_2-(C_d)(C)_3$ group has a lower barrier to internal rotation than for the trans isomer (see Figure S1 of the Supporting Information). Unfortunately, unlike alkenes, no systematic grouping of cis contributions seems to be possible for entropies.

For heat capacities, the cis corrections vary between −4.5 and 4.4 J mol^{-1} K^{-1}. There is a clear correlation between the cis contribution and the number of substituents on the alkylic C_2 carbon atom, whereas the substituents on the C_1 allylic carbon atom only have a minor influence. Therefore, no differentiation is made between the C_1 substituents. The cis corrections, averaged out for varying C_1 per type of C_2 substituent, are shown in Table 10.

3.3. Hydrogen Bond Increments for Hydrocarbon Radicals. Hydrogen bond increments for the calculation of radical thermochemistry, which are particularly useful for resonance-stabilized radicals, are given in Table 11. According to eqs 13 and 14, these HBIs are calculated directly from the difference between the ab initio value for the radical and the group additively predicted value for the parent molecule. Following Lay et al.,[38] the HBIs are denoted by a short-hand structure in which a J indicates the radical character of the preceding carbon atom, such as RCCJ for a primary alkyl radical, or by trivial names such as ALLYL_S for a secondary allylic radical. Radical-specific NNIs cannot be accounted for explicitly within

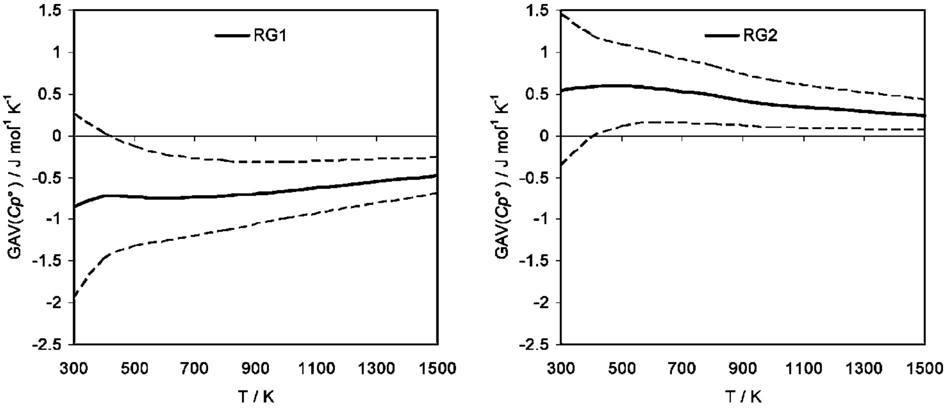


Figure 7. NNI corrections for the $C_p°$ of hydrocarbon radicals as a function of temperature (bold lines) and 97.5% confidence intervals (dashed lines).

TABLE 10: Allylic cis Contributions to the Entropy and Heat Capacity for Varying Substituents on Allylic Radicals (J mol^{-1} K^{-1})

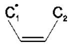
	S°(298K)			C_p° (independent of C_1 substitution)						
	$C_1-(H)_2$	$C_1-(C)(H)$	$C_1-(C)_2$	300	400	500	600	800	1000	1500
$C_2-(C_d)(H)_3$	+2.7	+1.0	−0.5	−3.0	−1.9	−1.3	−1.0	−0.7	−0.5	−0.3
$C_2-(C_d)(C)(H)_2$	−2.0	+0.7	−12.4	−3.7	−1.7	−0.5	0.2	0.8	0.9	0.7
$C_2-(C_d)(C)_2(H)$	−4.0	−7.2	−9.1	−4.5	−0.2	2.5	3.8	4.4	3.9	2.3
$C_2-(C_d)(C)_3$	+0.8	+1.7	−13.3	1.1	−0.4	−1.6	−2.3	−2.6	−2.4	−1.6

TABLE 11: Hydrogen Bond Increments for the Calculation of S° and C_p° of Radicals[a] (J mol^{-1} K^{-1})

		C_p°						
HBI	S°(298K)	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
CCJ	8.26	1.40	−1.78	−4.60	−7.03	−10.96	−13.93	−18.51
RCCJ	11.31	−2.31	−3.56	−5.39	−7.39	−11.15	−14.14	−18.79
ISOBUTYL	10.81	0.10	−2.21	−4.63	−6.98	−11.05	−14.20	−18.98
NEOPENTYL	15.34	1.15	−1.52	−4.42	−7.08	−11.40	−14.52	−18.95
CCJC	12.17	−7.35	−9.54	−11.20	−12.54	−14.76	−16.57	−19.76
RCCJC	16.92	−6.19	−8.45	−10.52	−12.23	−14.94	−16.94	−20.18
RCCJCC	23.49	−7.42	−9.22	−10.82	−12.38	−15.18	−17.37	−20.82
TERTALKYL	28.26	−11.16	−13.90	−15.41	−16.46	−18.01	−19.23	−21.32
VIN	5.51	0.18	−2.19	−4.91	−7.38	−11.30	−14.15	−18.62
VINS	7.99	−1.25	−4.00	−6.50	−8.64	−12.03	−14.57	−18.71
ALLYL_P	−9.16	−3.26	−2.67	−3.39	−4.74	−7.84	−10.57	−14.99
ALLYL_S	−6.00	−3.69	−4.82	−6.10	−7.43	−9.99	−12.15	−15.77
ALLYL_T	3.56	−11.85	−13.73	−14.76	−15.27	−15.79	−16.29	−17.68
BENZYL_P	−14.56	3.03	2.59	0.72	−1.57	−5.84	−9.21	−14.37
BENZYL_S	−7.09	−4.76	−4.66	−5.53	−6.75	−9.21	−11.39	−15.20
BENZYL_T	0.77	−9.20	−11.17	−12.37	−13.14	−14.17	−15.10	−17.13
C≡CJ	9.64	−0.17	−5.10	−8.43	−10.70	−13.65	−15.70	−19.13
C≡CCJ	3.58	1.97	−0.13	−2.73	−5.25	−9.59	−12.96	−18.14
C≡CCJC	13.23	−2.81	−4.56	−6.61	−8.58	−12.02	−14.76	−19.14
C≡CCJC2	19.05	−5.93	−9.87	−12.46	−14.13	−16.27	−17.82	−20.48
C=CJC=C	11.76	−1.17	−6.23	−10.58	−13.44	−16.13	−17.12	−18.33
C=CCJC=C(DIALLYL)	−21.23	−10.54	−8.38	−7.15	−6.74	−7.38	−8.70	−11.75
C≡CC=CJ	5.89	−0.57	−2.86	−5.32	−7.58	−11.28	−14.11	−18.58
C≡CC=CJC/CCJ=CC≡C	10.53	−3.96	−6.06	−8.07	−9.88	−12.83	−15.17	−19.05
C≡CCJC≡C (DIPROPARGYL)	7.71	−1.71	−4.51	−7.12	−9.25	−12.54	−15.06	−19.11
PHENYL	4.96	−1.49	−3.94	−6.33	−8.48	−11.90	−14.51	−18.79
C=CJC≡C	18.25	6.47	1.68	−2.34	−5.50	−9.97	−13.10	−17.92
C=CCJC≡C/C≡CC=CCJ	−6.21	−3.81	−4.96	−6.31	−7.61	−10.01	−12.07	−15.61
C≡CCJ(C≡C)C≡C	3.71	−0.51	−3.26	−5.93	−8.14	−11.62	−14.35	−18.69
C=CCJ(C≡C)C=C	−19.33	−11.19	−8.54	−7.46	−7.24	−8.00	−9.28	−12.03
(C6H5)CJ=C	2.15	3.46	0.37	−2.79	−5.47	−9.26	−11.78	−15.56
C≡CCJ(C6H5)	−10.52	3.65	1.88	−0.44	−2.75	−6.68	−9.74	−14.51
C=CCJ(C6H5)	−24.35	−1.49	−1.44	−2.15	−3.25	−5.63	−7.80	−11.52
C≡CCJ(C6H5)C	−4.26	−3.05	−5.60	−7.58	−9.09	−11.32	−13.06	−16.13
C=CCJ(C6H5)C	−25.09	−3.18	−4.01	−5.01	−5.98	−7.67	−9.04	−11.11
C=CCJ(C6H5)C≡C	−26.23	−2.30	−2.82	−3.67	−4.60	−6.31	−7.75	−10.05
C=CCJ(C6H5)C=C	−35.99	−3.39	−2.03	−1.78	−2.11	−3.43	−4.95	−7.93
C=CCJ(C=C)−C=C	−32.59	−8.37	−6.20	−4.92	−4.45	−4.88	−5.92	−8.42

[a] "J" indicates the presence of a radical on the preceding carbon atom.

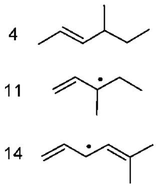
the HBI framework. Only the non-nearest-neighbor interactions present in the parent molecule are accounted for.

The 25 HBI structures introduced by Lay et al.[38] were not sufficient to describe the wide variety in our set of radicals. Hence, 15 new HBI structures were introduced, as has been done previously for standard enthalpies of formation.[9] The HBI values reported in this work are almost all within 6 J mol^{-1} K^{-1} of the results of Lay et al.[38] (see Table S16 of the Supporting Information). However, for secondary and tertiary radicals large differences are observed, with entropy HBI values up to 25 J mol^{-1} K^{-1} larger than the value of Lay et al.[38] These differences are much larger than the MAD of 1.3 J mol^{-1} K^{-1} on the GA prediction of the entropy of the parent molecules (see Table S6 of the Supporting Information). Hence, the differences cannot be attributed to the GA prediction for the parent molecule. Analysis of the different contributions to the HBI value reveals that the main difference originates from the contribution of the internal rotations about the bonds adjacent to the radical center. The barriers for these internal rotations, as calculated in this work, are consistently smaller than the values reported by Lay et al.[38] E.g., for the ALLYL_S and ALLYL_T increment, the barriers to internal rotation for the methyl rotors on the radical center are both taken as 8.8 kJ mol^{-1} by Lay et al.,[38] the same value for secondary and tertiary radicals, while in this study respectively 5.3 and 1.4 kJ mol^{-1} are found. The lower barriers in this work result in a higher entropy for the radical, leading to a higher HBI value. Moreover, for the benzylic

TABLE 12: Difference between Group Additively Predicted and Ab Initio Calculated Values for the Group Additivity Test Set (J mol^{-1} K^{-1})

			C_p°						
no.	species	S°(298K)	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
1	3-methylpentane	−3.1	3.5	2.6	1.8	1.2	0.6	0.4	0.3
2	2-methylbutane	−1.2	1.3	0.9	0.5	0.2	0.1	0.1	0.2
3	2-methylpent-2-ene	−3.9	4.8	4.2	2.9	1.8	0.5	−0.1	−0.4
4	trans-4-methylhex-2-ene	6.3	−4.4	−4.8	−3.7	−2.6	−1.3	−0.8	−0.3
5	but-2-yne	−0.1	−0.5	0.1	0.3	0.3	0.2	0.1	0.0
6	pent-1-yne	−1.7	3.1	1.6	0.8	0.4	0.1	0.1	0.1
7	1-phenylprop-1-ene	−1.6	−0.3	0.0	0.1	0.1	0.2	0.1	0.1
8	pent-3-yl	−1.0	3.9	2.0	1.1	0.7	0.5	0.4	0.3
9	pent-2-en-3-yl	−0.4	1.0	0.9	0.7	0.6	0.4	0.3	0.2
10	pent-2-yne-4-yl	2.2	−0.9	0.4	0.7	0.7	0.3	0.0	−0.4
11	3-methylpent-1-en-3-yl	5.5	−0.8	−2.5	−3.0	−2.9	−2.3	−1.7	−0.7
12	2-methylpenta-1,4-dien-3-yl	−3.2	2.6	3.1	2.9	2.5	1.8	1.3	0.8
13	hexa-1,4-dien-3-yl	−1.7	0.6	1.0	1.0	0.9	0.6	0.4	0.2
14	5-methylhexa-1,4-dien-3-yl	−8.4	2.7	4.4	4.3	3.7	2.5	1.7	0.8
			All Species						
	MAD	2.9	2.2	2.0	1.7	1.3	0.8	0.5	0.3
	rms	3.7	2.7	2.6	2.2	1.7	1.1	0.8	0.4
	MAX	8.4	4.8	4.8	4.3	3.7	2.5	1.7	0.8
			Radicals Only						
	MAD	3.2	1.8	2.0	1.9	1.7	1.2	0.8	0.5
	rms	4.1	2.1	2.4	2.4	2.1	1.5	1.1	0.5
	MAX	5.5	3.9	4.4	4.3	3.7	2.5	1.7	0.8

SCHEME 1: : *trans*-4-Methylhex-2-ene and the Radicals 3-Methylpent-1-en-3-yl and 5-Methylhexa-1,4-dien-3-yl (numbering as indicated in Table 12)



HBIs (BENZYL_P, _S, and _T) Lay et al.[38] apparently did not add the Rln2 contribution for the degeneracy of the electronic ground state to the entropy, which explains an extra 5.7 J mol^{-1} K^{-1} of the difference between Lay's values and this work for these HBIs.

The HBIs for the entropy are positive for alkyl radicals, corresponding to an entropy increase from parent molecule to radical despite the loss of an H atom. This increase in entropy is due to the fact that the formation of a radical center is accompanied by a decrease in the barrier to internal rotation about the adjacent σ bonds. For the formation of radicals with strong resonance stabilization such as allylic and benzylic radicals, the entropy decreases due to the loss of one or more internal degrees of freedom, such as the rotation about the C°−C_d bond.

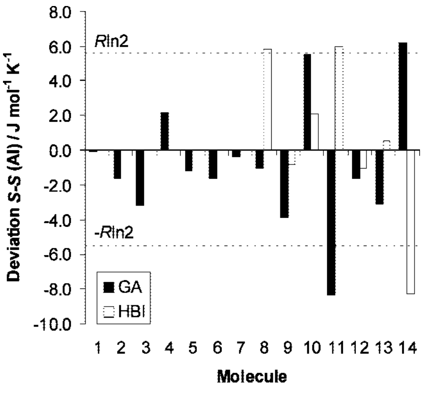


Figure 8. Deviation of the group additive entropy from the ab initio entropy. The dotted lines indicate the deviation for which the equilibrium coefficient is affected by a factor of 2 (J mol^{-1} K^{-1}).

For heat capacities, the HBI values are generally negative, accounting for the loss of the contributions of three rovibrational modes to the heat capacity. The most negative values pertain to structures with alkyl substituents on the radical center. The rotational barriers of the alkyl substituents on the radical center decrease upon radical formation, resulting in a decrease in C_p° contribution from basically R, the fully developed contribution of a harmonic oscillator to C_p°, to $R/2$, the contribution of a free rotor. Hence, the heat capacity decreases, with the magnitude of the decrease related to the number of alkyl substituents on the radical center of the HBI structure.

Some C_p°-HBIs are positive, however, which relates to an increase in heat capacity upon radical formation. For these structures, a low-frequency mode is present in the radical, which has a fully developed contribution to C_p° already at low temperatures, whereas the moderate-frequency modes in the parent molecule do not yet provide their full contribution to C_p°. This is the case for, starting with the most positive, the HBIs C=CJC≡C, CH≡CCHJ(C6H5), BENZYL_P, (C6H5)CJ=CH2, C'CCJ, CCJ, *C*=CJC=C, NEOPENTYL, and ISOBUTYL.

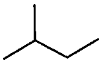
The temperature dependence of the HBIs for C_p°s is negative: almost all HBIs decrease with temperature (see Figure S2 of the Supporting Information). This can be explained as follows. There are three rovibrational modes in the parent molecule that are lost on radical formation. The contributions to C_p° for these modes increase with temperature, which explains the general decrease of the HBIs with temperature as the HBIs are defined as C_p°(radical) − C_p°(parent molecule). Only for some allylic and benzylic structures an increase in HBI value is observed, attaining a maximum between 400 and 600 K before decreasing with temperature. This is caused by the loss of some specific internal rotations in the parent molecule on radical formation, particularly the internal rotations about the bonds at the

TABLE 13: Difference between the Value Predicted by the HBI Method and ab Initio Calculated Value for the Radicals from the Group Additivity Test Set (J mol^{-1} K^{-1})

			C_p°						
no.	species	S°(298K)	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
8	pent-3-yl	5.8	3.2	1.7	1.1	0.7	0.3	−0.1	−0.4
9	pent-2-en-3-yl	−0.8	1.4	1.2	1.0	0.8	0.5	0.4	0.3
10	pent-2-yne-4-yl	2.1	0.1	1.5	1.9	1.7	1.1	0.6	0.0
11	3-methylpent-1-en-3-yl	6.0	−0.8	−2.4	−2.9	−2.8	−2.3	−1.7	−0.8
12	2-methylpenta-1,4-dien-3-yl	−1.0	−1.0	−0.9	−0.5	−0.2	0.3	0.5	0.5
13	hexa-1,4-dien-3-yl	0.6	−3.0	−3.0	−2.4	−1.8	−0.9	−0.5	−0.2
14	5-methylhexa-1,4-dien-3-yl	−8.2	−2.6	−0.6	1.1	2.0	2.5	2.3	1.4
	MAD	3.5	1.7	1.6	1.5	1.4	1.1	0.9	0.5
	rms	4.5	2.0	1.8	1.7	1.7	1.4	1.1	0.6
	MAX	6.0	3.2	1.7	1.9	2.0	2.5	2.3	1.4

(forming) radical center that are lost due to resonance stabilization.

3.4. Application and Validation of the GA Method. A validation of the group additivity method is provided by comparing values predicted by group additivity and the HBI method with ab initio calculated values, for 14 various species not included in the training set. First, the use of the GAV is illustrated by means of sample calculations of the entropy of 2-methylbutane and hexa-1,4-dien-3-yl. In 2-methylbutane there are three $C-(C)(H)_3$ groups, one $C-(C)_2(H)_2$ group, one $C-(C)_3(H)$ group, and moreover one alkane gauche (AG) interaction. Therefore, the intrinsic entropy $S_{\text{int}} = 3(127.20) + 39.89 + (-48.30) + (-0.70) = 372.49$ J mol^{-1} K^{-1}. Because of the presence of three methyl rotors and the absence of external symmetry, the global symmetry number is 3^3, which yields for the entropy $S = S_{\text{int}} - R\ln 3^3 = 372.49 - 27.40 = 345.09$ J mol^{-1} K^{-1}, which agrees very well with the ab initio calculated value of 346.25 J mol^{-1} K^{-1}.



For a group additive prediction of the entropy of the hexa-1,4-dien-3-yl radical the represented canonical structure must be used, as the radical group $C^\circ-(C_d)_2(H)$ in this canonical structure is able to describe all radical delocalization. For the other canonical structures, this is not the case, as the respective radical groups $C^\circ-(C_d)(H)_2$ and $C^\circ-(C_d)(C)(H)$ only describe one double bond and do not describe the resonance contribution of the second double bond. The intrinsic entropy is made up from the contributions of the groups $C_d-(H)_2 + 2(C_d-(C^\circ)(H)) + C^\circ-(C_d)_2(H) + C_d-(C)(H) + C-(C_d)(H)_3$. This yields, with the radical adjacent group $C_d-(C^\circ)(H)$ set equal to the non-radical hydrocarbon equivalent $C_d-(C)(H)$, $S_{\text{int}} = 115.76 + 2(32.91) + 16.49 + 32.91 + 127.20 = 358.18$ J mol^{-1} K^{-1}. As $\sigma_{\text{ext}} = 1$ and $\sigma_{\text{int}} = 3$ for the methyl rotor, the entropy is $S = S_{\text{int}} - R\ln 3 = 358.18 - 9.13 = 349.05$ J mol^{-1} K^{-1}, in excellent agreement with the ab initio calculated value of 350.7 J mol^{-1} K^{-1}. Similarly, for the heat capacity one obtains $C_p^\circ = 20.59 + 2(18.44) + 17.36 + 18.44 + 24.95 = 118.2$ J mol^{-1} K^{-1}, while the ab initio calculated value amounts to 117.6 J mol^{-1} K^{-1}.

To illustrate the use of the HBI method, the entropy of the same radical is calculated. The intrinsic entropy of the parent hydrocarbon hexa-1,4-diene is first calculated using group additivity. This yields $S_{\text{int}} = C_d-(H)_2 + 3(C_d-(C)(H)) + C-(C_d)_2(H)_2 + C-(C_d)(H)_3 = 115.76 + 3(32.91) + 39.93 + 127.20 = 381.62$ J mol^{-1} K^{-1}. Next, to obtain the intrinsic entropy of the radical, the C=CCJC=C HBI is added to the intrinsic entropy of the parent molecule, which gives $381.62 + (-21.23) = 360.39$ J mol^{-1} K^{-1}. Subtracting $R \ln 3$ then yields the resulting entropy of 351.26 J mol^{-1} K^{-1}, which is only slightly higher than the ab initio value of 350.7 J mol^{-1} K^{-1}.

The validation set for the group additive method consists of seven hydrocarbons and seven hydrocarbon radicals, representing all types of compounds, including species with strong resonance stabilization. The differences between GA prediction and ab initio calculation for these species are given in Table 12. The actual values for S° and C_p° can be retrieved from Table S17 of the Supporting Information. For entropies, the GA method predicts values within 5 J mol^{-1} K^{-1} of the calculated values, except for species 4, 11, and 14 from Table 12 (see Scheme 1).

The latter radicals exhibit resonance stabilization, which often hampers the accuracy of a group additive prediction. The individual deviations are shown in Figure 8.

Also for heat capacities, the predictions are within 5 J mol^{-1} K^{-1} of the ab initio value over the entire temperature range.

For radicals, also the HBI method is tested (see Table 13). In general, the results for entropies and heat capacities are comparable to the GA method. Only for the entropy of the pent-3-yl radical the difference the GA method performs slightly better than the HBI method as compared to the ab initio values. The individual deviations on the entropy are compared with the group additive results in Figure 8.

From these results, it can be concluded that the GA method predicts entropies and heat capacities within ~5 J mol^{-1} K^{-1} of the ab initio calculations. Using as criterion a maximum deviation of a factor of 2 on the equilibrium coefficient, these deviations can be considered acceptable. For entropies, this criterion involves a maximum error of $R\ln 2$ (5.8 J mol^{-1} K^{-1}), which is fulfilled by 12 of the 14 species. For heat capacities, the effect of an error ΔC_p° on the Gibbs energy is, assuming that it is calculated from the value at 298 K:

$$\Delta G = (T - 298)\Delta C_p^\circ - T\Delta C_p^\circ \ln\left(\frac{T}{298}\right) \qquad (15)$$

The effect on the equilibrium coefficient is clearly temperature-dependent. At 1000 K, assuming that the error on C_p° is temperature-independent, the equilibrium coefficient will only be affected by a factor of 2 for ΔC_p° errors larger than 11.3 J mol^{-1} K^{-1}, which does not occur for any species in the set. At

1500 K, the maximal acceptable deviation is reduced to 7.1 J mol^{-1} K^{-1}, which still holds for all species in the set.

4. Conclusions

For the prediction of the thermochemistry of the reactive species in large hydrocarbon radical reaction networks, two schemes are presented filling the gap in the available data required for the prediction of thermochemistry for radical species. A database of entropies and heat capacities for 265 compounds has been constructed, using ideal gas statistical thermodynamics based on B3LYP/6-311G(d,p) calculations, including corrections for hindered rotation for all internal rotors. The computational approach is shown to agree well with experimental values, with mean absolute deviations between calculation and experiment below 2 J mol^{-1} K^{-1} for entropies $S°$ at 298 K and heat capacities $C_p°$ at 298 K and higher temperatures up to 693 K.

Consistent with previously determined GAVs for standard enthalpies of formation $\Delta_f H°(298K)$,[9] a set of 95 group additive values for $S°$ and $C_p°$ is derived from this database. For a total of 46 groups GAVs have been determined for the first time, including 25 radical groups. Without significant loss of accuracy, a 3-fold reduction of the number of GAVs to be determined for the prediction of radical thermochemistry could be achieved by setting the GAVs of the radical-adjacent groups equal to the GAVs of the corresponding nonradicalar hydrocarbon groups.

The large database allowed for an in-depth analysis of non-nearest-neighbor effects, which are shown to improve the accuracy. The substituent effects on the magnitude of cis interaction corrections could be explained on the basis of the differences in rotational potential energy profiles between cis and trans isomers. Radical gauche corrections for $S°$ and $C_p°$, which have never been determined before, differ significantly from zero and improve the group additive predictions for strongly substituted alkyl radicals. Next to GAVs, also hydrogen bond increments for radicals have been determined, which are useful for resonance-stabilized radicals.

The obtained group additive values are validated in a set of 14 widely different hydrocarbons and hydrocarbon radicals. Comparison of group additive prediction with ab initio calculation shows that entropy and heat capacity are predicted within ~5 J mol^{-1} K^{-1} for 11 of the 14 molecules considered and that only for two species an error on the equilibrium coefficient of more than a factor 2 is induced. Hence, the GAVs reported in this work can be reliably applied for the prediction of the thermochemistry in large hydrocarbon reaction networks, combining an extremely fast prediction with a wide application range. In particular, this work strongly extends the application range for the prediction of entropy and heat capacity of hydrocarbon radicals.

Acknowledgment. We are grateful for financial support from the Fund for Scientific Research-Flanders (F.W.O.-Vlaanderen). M.K.S. holds a Ph.D. grant of the Institute for the Promotion of Innovation through Science and Technology in Flanders (IWT-Vlaanderen).

Notation

List of Symbols

A_k, cosine Fourier expansion coefficient for $V(\psi)$, J mol^{-1}
B_k, sine Fourier expansion coeffient for $V(\psi)$, J mol^{-1}
$C_p°$, standard heat capacity
$I_{m,red}$, reduced moment of inertia for internal rotation, kg m^2
k_B, Boltzmann constant, J K^{-1}
n_{opt}, number of optical isomers
P, pressure, Pa
q, molecular partition function
Q, canonical partition function
$S°$, standard entropy, J mol^{-1} K^{-1}
$S°_{int}$, intrinsic entropy, J mol^{-1} K^{-1}
T, temperature, K
$V(\psi)$, potential energy profile for internal rotation, J mol^{-1}
σ, symmetry number (ext, external; int, internal)

Acronyms

1D-HR, uncoupled hindered internal rotation
AG, alkane gauche
GAV, group additive value
HBI, hydrogen bond increment
HO, harmonic oscillator
RG, radical gauche

Supporting Information Available: Comparison between experimental and ab initio calculated entropies, and those obtained by Bond (Tables S1 and S2), comparison between experimental and ab initio calculated heat capacities at 298 K and higher temperatures (Tables S3 and S4), ab initio determined entropies and heat capacities for all species in the database (Table S5), differences between group additive and ab initio calculated entropy and heat capacities for all species in the database (Table S6), comparison between Benson GAVs and our GAVs for alkane, alkene, alkyne, aromatic, and radical groups (Tables S7−S9, S11, S12, and S15), determination of alkene cis corrections (Table S10), influence of group additive modeling approach on the deviation between group additive prediction and ab initio values for radicals (Tables S13 and S14), comparison between the HBI values determined in this work and the values of Lay et al. (Table S16), entropies and heat capacities of the group additive test set (ab initio values, group additive, and HBI predictions (Table S17)), potential energy profile for the *tert*-butyl internal rotation in *cis*- and *trans*-4,4-dimethylpent-2-en-1-yl (Figure S1), HBI values for the heat capacity as function of temperature (Figure S2), geometries of all species, and Fourier expansions of the energy profiles for internal rotation. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP807526N