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Thermochemical Data and Additivity Group Values for Ten Species of o-Xylene Low-Temperature Oxidation Mechanism

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S *Supporting Information*

ABSTRACT: *o*-Xylene could be a good candidate to represent the family of aromatic hydrocarbons in a surrogate fuel. This study uses computational chemistry to calculate standard enthalpies of formation at 298 K, $\Delta_f H°(298\ K)$, standard entropies at 298 K, $S°(298\ K)$, and standard heat capacities $C_p°(T)$ over the temperature range 300 K to 1500 K for ten target species present in the low-temperature oxidation mechanism of *o*-xylene: *o*-xylene (**1**), 2-methylbenzyl radical (**2**), 2-methylbenzylperoxy radical (**3**), 2-methylbenzyl hydroperoxide (**4**), 2-(hydroperoxymethyl)benzyl radical (**5**), 2-(hydroperoxymethyl)benzaldehyde (**6**), 1-ethyl-2-methylbenzene (**7**), 2,3-dimethylphenol (**8**), 2-hydroxybenzaldehyde (**9**), and 3-hydroxybenzaldehyde (**10**). $\Delta_f H°(298\ K)$ values are weighted averages across the values calculated using five isodesmic reactions and five composite calculation methods: CBS-QB3, G3B3, G3MP2, G3, and G4. The uncertainty in $\Delta_f H°(298\ K)$ is also evaluated. $S°(298\ K)$ and $C_p°(T)$ values are calculated at B3LYP/6-311G(d,p) level of theory from molecular properties and statistical thermodynamics through evaluation of translational, rotational, vibrational, and electronic partition functions. $S°(298\ K)$ and $C_p°(300\ K)$ values are evaluated using the rigid-rotor-harmonic-oscillator model. $C_p°(T)$ values at $T \geq 400\ K$ are calculated by treating separately internal rotation contributions and translational, external rotational, vibrational, and electronic contributions. The thermochemical properties of six target species are used to develop six new additivity groups taking into account the interaction between two substituents in ortho (ORT/CH2OOH/ME, ORT/ET/ME, ORT/CHO/OH, ORT/CHO/CH2OOH) or meta (MET/CHO/OH) positions, and the interaction between three substituents (ME/ME/OH123) located one beside the other (positions numbered 1, 2, 3) for two- or three-substituted benzenic species. Two other additivity groups are also developed using the thermochemical properties of benzenic species taken from the literature: the C/CB/H2/OO and the CB/CO groups. These groups extend the capacities of the group additivity method to deal with substituted benzenic species.
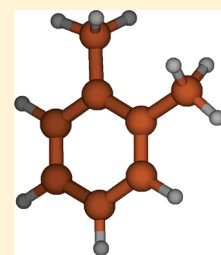
1. INTRODUCTION

Aromatic hydrocarbons are automotive and jet fuel components. Their percentage in mass in a European gasoline, a Californian reformulated gasoline, a diesel fuel, and a jet fuel is 35%, 31%, 30%, and 15%, respectively.[1] Useful properties of aromatic hydrocarbons and their negative impact on the environment and health have been mentioned in our recent articles.[2,3] Experimental and thermokinetic modeling studies of surrogate fuel combustion have been carried out to understand the mechanisms of pollutant and toxic compound formation.[4−8] An ideal surrogate fuel is composed of molecules which represent each family of compounds included in a real fuel: alkanes, aromatic hydrocarbons, cyclanes, alkenes, and oxygenated compounds. In the aromatic hydrocarbon family, the class of alkylbenzenes is of prime importance because the percentages in weight of this class in a European gasoline, diesel fuel, and jet fuel are 32%, 9%, and 24%, respectively.[1] Xylenes are a part of the alkylbenzenes present in a real fuel (the sum of their percentages in weight is about 10% in a European gasoline[1]) and hence could be good candidates to represent the family of aromatic hydrocarbons in a surrogate fuel.

A detailed thermokinetic model for low temperature oxidation of *o*-xylene is currently being elaborated in our laboratory. It is partly based on the reaction scheme shown in Figure 1. This reaction scheme shows the formation of oxidation products analyzed in a rapid compression machine (RCM) study[9,10] at 704 K and in a flow reactor study[11] at 1150 K. *o*-Xylene (**1**), 2,3-dimethylphenol (**8**), 2-hydroxybenzaldehyde (**9**), and 3-hydroxybenzaldehyde (**10**) were measured between the two stages of an RCM autoignition experiment under the following conditions: 15.6 bar, 704 K, stoichiometric fuel/O_2/inert mixture, ratio O_2/inert = 0.37. The 1-ethyl-2-methylbenzene molecule (**7**) is one of the major oxidation products in the flow reactor study performed at 1150 K, 1 bar, with an *o*-xylene/O_2/N_2 mixture of equivalence ratio 1.1 and a mole fraction of N_2 higher than 0.97. The species **2** to **6** are assumed to be reaction intermediates in the reaction scheme.

The group additivity method (GAM) is an inexpensive, straightforward, and often accurate calculation method to estimate
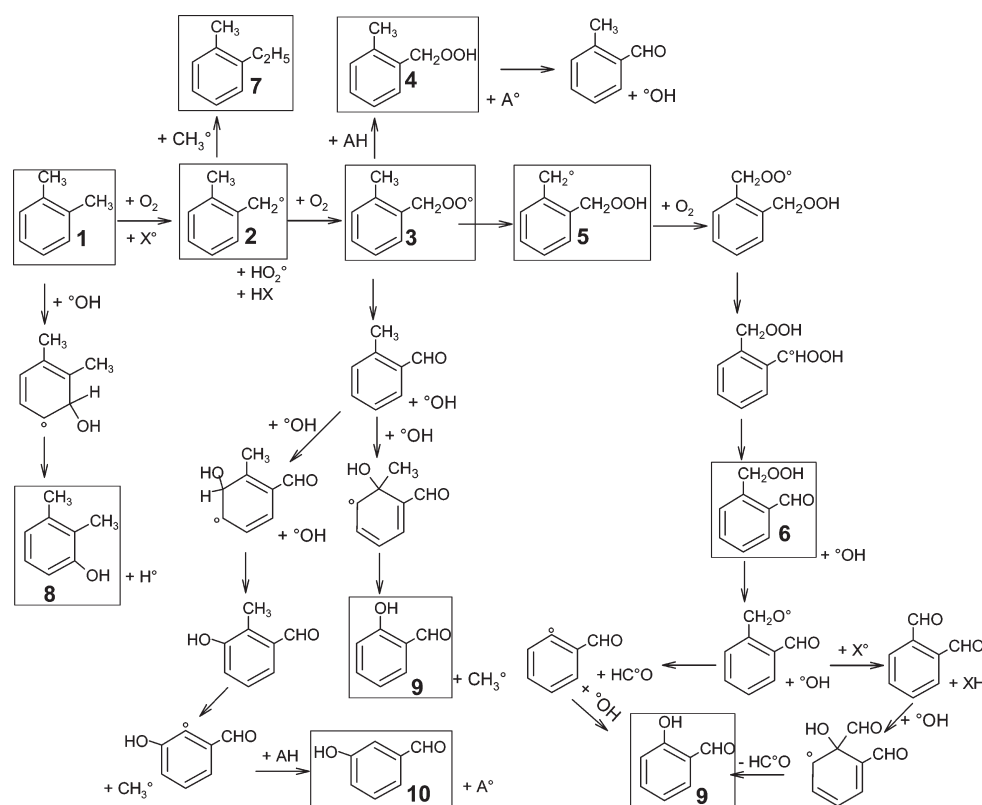
Figure 1. Reaction scheme of low-temperature *o*-xylene oxidation, showing the structure of target species. X° represents any radical present in the pool of radicals, and AH represents a species with a labile H atom such as an aldehyde.

thermochemical properties of large molecules and radicals.[12−14] It serves as valuable estimation technique for researchers whose work involves generation of thermochemical databases for chemical species involved in combustion processes.[15−21] Estimation of thermochemical properties based on GAM can be performed using the THERM program.[22−24] However, because of missing additivity groups (AG) in the THERM AG database, thermochemical data of many species cannot be estimated by this method. The replacement of a missing AG by an AG of similar structure can be a coarse solution in this case; however, a more rigorous and accurate solution consists of resorting to quantum chemistry methods.[25] Thus, the first aim of this work is to determine thermochemical data, which are impossible to evaluate with GAM, using ab initio and density functional density methods. The second aim of this work is to deduce missing group contributions to thermochemical properties from the thermochemical data evaluated in this work and hence to complete the THERM AG database and extend the capacities of the GAM. The present article is the third of an ongoing series devoted to the generation of thermokinetic data for alkylbenzenes.[2,26]

In this work, standard enthalpy of formation at 298 K, $\Delta_f H°(298 \text{ K})$, standard entropy at 298 K, $S°(298 \text{ K})$, and $C_p°(T)$ over the temperature interval 300 K to 1500 K, of ten target species present in the *o*-xylene reaction scheme of Figure 1 and listed in Table 1, are calculated using quantum chemistry methods. $\Delta_f H°(298 \text{ K})$ values are evaluated with five composite methods, a set of five isodesmic reactions, and statistical thermodynamics. To our knowledge, $\Delta_f H°(298 \text{ K})$ of 2-methylbenzylperoxy radical (**3**), 2-(hydroperoxymethyl)benzyl radical (**5**), and 2-(hydroperoxymethyl)benzaldehyde (**6**) have been determined

for the first time. $S°(298 \text{ K})$ and $C_p°(T)$ are determined from molecular properties calculated using the B3LYP density functional method, the 6-311G(d,p) basis set, and statistical thermodynamics. The contributions of internal rotors to $C_p°(T \geq 400 \text{ K})$ are calculated using direct integration over energy levels of the internal rotation potential energy curve. To our knowledge, $S°(298 \text{ K})$ and $C_p°(T)$ of species **3−7**, **9**, and **10** have been determined for the first time. In the next paragraphs we report literature thermochemical data for the target species, obtained either by quantum chemistry calculations or by additivity methods. The thermochemical properties of target species **4** and **6−10** have been used to develop six interactions AG for two substituents in ortho or meta positions, and three substituents located one beside the other in substituted benzenic species. Two other central AG have been also developed using the thermochemical properties of benzenic species taken from the literature.

da Silva et al.[27] have calculated $\Delta_f H°(298 \text{ K})$ of *o*-xylene using the G3X and G3SX composite methods and the atomization reaction of the target species and have reported values of 3.96 and 4.05 kcal mol⁻¹, respectively. Santos et al.[28] have determined a value of 4.52 kcal mol⁻¹ for $\Delta_f H°(298 \text{ K})$ of *o*-xylene using the extended Laidler bond additivity method. Taskinen[29] has reported a value of 4.47 kcal mol⁻¹ for $\Delta_f H°(298 \text{ K})$ of *o*-xylene using the G3(MP2)//B3LYP composite method, the atomization reaction of the target species, and taking into account a structure-dependent correction term. Battin-Leclerc et al.[30] have estimated $\Delta_f H°(298 \text{ K})$ of *o*-xylene to be 4.5 kcal mol⁻¹ using THERGAS[31] software based on a GAM.

$\Delta_f H°(298 \text{ K})$ of 2-methylbenzyl radical (**2**) has been calculated by Orlov et al.[32] using the benzyl-CH₂−H bond dissociation

593

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Table 1. Number, Name, and Structure of Target Species

number	name (this work)	other name	structure
1	*o*-xylene	1,2-dimethylbenzene[28]	
2	2-methylbenzyl radical	*o*-methylbenzyl radical[27,30]	
3	2-methylbenzylperoxy radical		
4	2-methylbenzylhydroperoxide		
5	2-(hydroperoxymethyl)benzyl radical		
6	2-(hydroperoxymethyl)benzaldehyde		
7	1-ethyl-2-methylbenzene		
8	2,3-dimethylphenol	methylcresol[30] 2,3-xylenol	
9	2-hydroxybenzaldehyde	2-formylphenol[38]	
10	3-hydroxybenzaldehyde	3-formylphenol[38]	

energy taken from Hayashibara et al.[33] study, the enthalpy of formation of *o*-xylene tabulated in Pedley et al.,[34] and a value of 52.10 kcal mol^{-1} for $\Delta_f H°(298\ \text{K})$ of the H atom. The obtained value of 39.79 kcal mol^{-1} was then refined using a bond dissociation energy from Tumanov et al.[35] study, leading to a value[36] of 40.42 kcal mol^{-1}. da Silva et al.[27] have recently determined thermochemical properties ($\Delta_f H°(298\ \text{K})$, $S°(298\ \text{K})$, and $C_p°(300\ \text{K} \leq T \leq 2000\ \text{K})$) of 2-methylbenzyl radical (named *o*-methylbenzyl radical in their article) using the G3X and G3SX composite methods. The $\Delta_f H°(298\ \text{K})$ value has been calculated using both the atomization reaction of the target species and the bond dissociation reaction *o*-xylene = *o*-methylbenzyl + H. The G3X $\Delta_f H°(298\ \text{K})$ deduced from the atomization reaction is evaluated to be 43.25 kcal mol^{-1} (42.75 kcal mol^{-1} for G3SX value), whereas the G3X $\Delta_f H°(298\ \text{K})$ using the bond dissociation reaction is calculated to be 43.83 kcal mol^{-1}. Compared to results obtained for *m*- and *p*-methylbenzyl radicals in the same study, the atomization and bond dissociation $\Delta_f H°(298\ \text{K})$ values of *o*-methylbenzyl radical differs notably: indeed the difference between the results obtained with both methods is 0.17 and 0.00 kcal mol^{-1} for *m*- and *p*-methylbenzyl radicals, respectively. This disagreement is possibly attributed to a too high experimental value of $\Delta_f H°(298\ \text{K})$ for *o*-xylene[37] (4.54 kcal mol^{-1}) compared to those of other xylene isomers (4.12 and 4.29 kcal mol^{-1} for *m*- and *p*-xylene, respectively). $S°(298\ \text{K})$

and $C_p°(300\ \text{K})$ of species **2** are calculated to be 83.924 and 31.143 cal K^{-1} mol^{-1}, respectively, with internal rotational modes treated as hindered rotors, based upon the results of relaxed B3LYP/6-31G(2df,p) rotor scans. Battin-Leclerc et al.[30] have calculated $\Delta_f H°(298\ \text{K})$ of *o*-methylbenzyl radical (**2**) to be 42.0 kcal mol^{-1} using THERGAS software based on a GAM.

Using THERGAS software, Battin-Leclerc et al.[30] have also estimated $\Delta_f H°(298\ \text{K})$ of 2-methylbenzylhydroperoxide (**4**) and 2,3-dimethylphenol (**8**) (named methylcresol in their article) to be −15.6 kcal mol^{-1} and −37.6 kcal mol^{-1}, respectively. Santos et al.[28] have determined a value of −0.26 kcal mol^{-1} for $\Delta_f H°(298\ \text{K})$ of species 1-ethyl-2-methylbenzene (**7**) using the extended Laidler bond additivity method. Gomez et al.[38] have calculated $\Delta_f H°(298\ \text{K})$ of species 2-hydroxybenzaldehyde (**9**) and 3-hydroxybenzaldehyde (**10**) (named 2- and 3-formylphenol in their article) using the composite G3(MP2)//B3LYP/6-31G(d) method and the atomization reaction of the target species or one isodesmic reaction. The values calculated with one isodesmic reaction (in principle more accurate than those calculated with the atomization reaction) are −57.77 and −52.01 kcal mol^{-1} for species **9** and **10**, respectively. The values determined with the atomization reactions are about 0.6 kcal mol^{-1} lower.

The article is organized as follows. Computational methods are reported in section 2, which is divided in two subsections:

$\Delta_f H°$(298 K) calculation (2.1) and $S°$(298 K) and $C_p°(T)$ calculations (2.2). The results are presented and discussed in section 3, which is divided in five subsections: geometries and vibrational frequencies (3.1), rotational barriers (3.2), $\Delta_f H°$(298 K) values (3.3), $S°$(298 K) and $C_p°$(300 K $\leq T \leq$ 1500 K) values (3.4), and additivity group values (3.5).

2. COMPUTATIONAL METHODS

Quantum chemistry calculations were performed using the GAUSSIAN03[39] and GAUSSIAN09[40] program suites. $\Delta_f H°$(298 K) were calculated using five composite calculation methods: CBS-QB3,[41,42] G3B3,[43] G3MP2,[44] G3,[45] and G4.[46] G3B3, G3MP2, and G3 methods have been assessed using 299 energies from the G2/97 test set including enthalpies of formation, ionization potentials, electron affinities, and proton affinities. The average absolute deviations from experiment for the 299 energies are 1.01, 1.30, and 0.99 kcal mol^{-1} for G3, G3MP2, and G3B3 methods, respectively compared to 1.48 kcal mol^{-1} for G2 method.[43] The maximal absolute deviations from experiment for the 299 energies of the G2/97 test set are close for G3 and CBS-QB3 (1.10 kcal mol^{-1}) methods, but the latter one is about three times faster than G3 method.[28] The G4 method, which modifies the G3 method in five ways, has been assessed on the 454 experimental energies of the G3/05 test set, and the average absolute deviation from experiment shows significant improvement from 1.13 kcal mol^{-1} for G3 method to 0.83 kcal mol^{-1} for G4 method.[46]

$S°$(298 K) and $C_p°(T)$ over the temperature range 300 K to 1500 K have been calculated using molecular properties obtained at B3LYP/6-311G(d,p) level of theory. The B3LYP/6-311G(d,p) level of theory is chosen because it has a somewhat larger basis set than the commonly used B3LYP/6-31G(d,p), and it is still reasonable for structure optimization and force constant calculation on the molecules in this study. Mebel et al.[47] have shown that this level of theory give similar energies to those obtained with higher levels of theory (G2M(RCC,MP2)) on a number of unsaturated peroxide and peroxy species. Byrd et al.[48] and Curtiss et al.[49] report that the B3LYP/6-31G(d,p) level of theory provides accurate structures for compounds with elements up to atomic number 10. Peterson et al.[50] recommend the use of B3LYP density functional method for geometry and frequencies in several of their CBS calculation methods. Hou et al.[51] have studied internal rotations in vinylcyclopropane and other species by using the B3LYP/6-311G(d,p), B3LYP/6-311+G(d,p), and B3LYP/6-311++G(d,p) levels of theory. They showed a good agreement between the experiment and the calculations for the general features of the internal rotation potential curves, the rotational barriers, the bond lengths, and the bond angles of the stationary-point structures. Sebbar et al.[52,53] have used the B3LYP/6-311G(d,p) level of theory to determine thermochemical properties of a number of vinyl hydroperoxides and peroxy radicals, as well as ethynyl, allyl, and phenyl hydroperoxides. A good agreement through a range of peroxy and peroxide species between B3LYP/6-311G(d,p) $\Delta_f H°$(298 K) values and values obtained with a number of high-level calculation methods, as well as experimental data has been shown by Sebbar et al.[54] They have determined in the same study[54] thermochemical properties, rotational barriers, bond energies, and group additivity values for a series of vinyl, phenyl, ethynyl, and allyl peroxides. G3B3,[43] G3MP2,[44] G3,[45] and G4.[46]

Total electronic energy at 0 K was corrected by adding the zero-point vibrational energy (ZPVE). Vibrational frequencies were scaled using appropriate scaling factors according to the level of theory used to obtain stationary points: 0.99[41] for CBS-QB3 method (B3LYP/6-311G(2d,d,p) level of theory), 0.96[43] for G3B3 method (B3LYP/6-31G(d) level of theory), 0.8929[44,45] for G3MP2 and G3 methods (HF/6-31G(d) level of theory), 0.9854[46] for G4 method (B3LYP/6-31G(2df,p) level of theory), and 0.967[55] at B3LYP/6-311G(d,p) level of theory. Standard enthalpy at 298 K, $H°$(298 K), was obtained by adding to the corrected total electronic energy at 0 K the thermal correction to enthalpy, which takes into account translational, rotational, vibrational, and electronic contributions to enthalpy at 298 K. Rotational conformers of the target species were identified, but only the conformer of lowest $H°$(298 K) was considered to determine the thermochemical properties of the target species.

2.1. $\Delta_f H°$(298 K) Calculation. $\Delta_f H°$(298 K) of a target species was calculated using the isodesmic reaction methodology with a set of five isodesmic reactions. An isodesmic reaction is an hypothetical reaction in which the bonds of the same type are conserved on both sides of the equation. By constructing an isodesmic reaction involving the target species and reference species with accurately known enthalpies of formation, $\Delta_f H°$(298 K) of the target species is obtained from the enthalpy of isodesmic reaction at 298 K and the $\Delta_f H°$(298 K) of the reference species as shown hereafter. Let us consider a target species TS involved in the isodesmic reaction i whose equation is TS + RS$_1$ = RS$_2$ + RS$_3$ where RS$_1$, RS$_2$, and RS$_3$ are reference species whose enthalpies of formation at 298 K $\Delta_f H°$(RS$_1$), $\Delta_f H°$(RS$_2$), $\Delta_f H°$(RS$_3$) are known. The standard enthalpy at 298 K of reference species noted, respectively, $H°$(RS$_1$), $H°$(RS$_2$), and $H°$(RS$_3$), are calculated by the same calculation method as that used for the target species. The enthalpy of reaction i $\Delta_r H°_i$ can be then expressed by eqs 1 and 2

$$\Delta_r H°_i = -H°(TS) - H°(RS_1) + H°(RS_2) + H°(RS_3)$$

(1)

$$\Delta_r H°_i = -\Delta_f H°(TS) - \Delta_f H°(RS_1) + \Delta_f H°(RS_2) + \Delta_f H°(RS_3)$$

(2)

where $H°$(TS) and $\Delta_f H°$(TS) are the enthalpy and the enthalpy of formation of the target species at 298 K, respectively. By equaling the two expressions of $\Delta_r H°_i$, the following expression of $\Delta_f H°$(TS) is obtained

$$\Delta_f H°(TS) = -\Delta_r H°_i - \Delta_f H°(RS_1) + \Delta_f H°(RS_2) + \Delta_f H°(RS_3)$$

(3)

where $\Delta_r H°_i$ is calculated by eq 1.

An isodesmic reaction provides a higher accuracy in the determination of $\Delta_f H°$(298 K). Indeed, the systematic errors arising from the inability of the calculation method to reproduce the true electronic structure tend to appear in both reactants and products and are partially canceled because of the conservation of bonds. Several previous studies showed that an accuracy near 0.5 kcal mol^{-1} can be obtained by this enthalpy determination based on isodesmic reaction methodology.[56−58]

The final $\Delta_f H°$(TS) value at 298 K of a target species TS is a weighted average across the values given by the five isodesmic reactions and the five calculation methods. The weights are the

595

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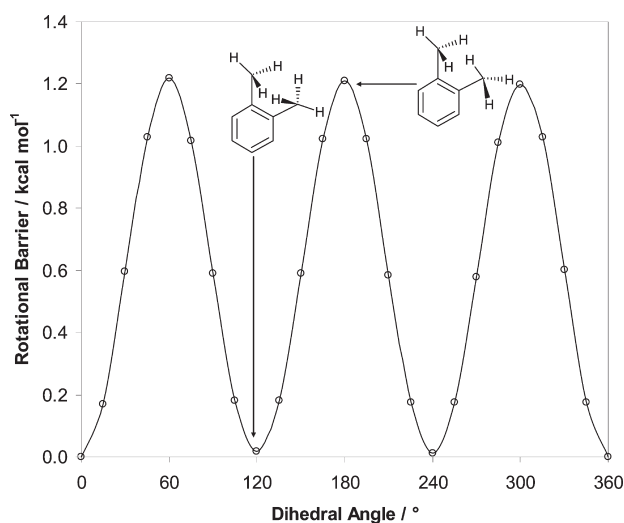
Figure 2. Barrier for internal rotation versus the dihedral angle in *o*-xylene (**1**): −CH₃ (○). Points are calculated values at the B3LYP/6-311G(d,p) level of theory.
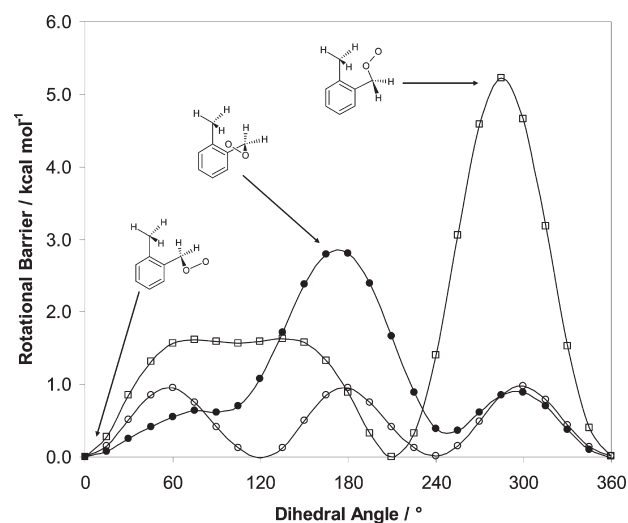

Figure 4. Barrier for internal rotation versus the dihedral angle in 2-methylbenzylperoxy radical (**3**): −CH₃ (○), −CH₂OO° (□), −OO° (●). Points are calculated values at the B3LYP/6-311G(d,p) level of theory.
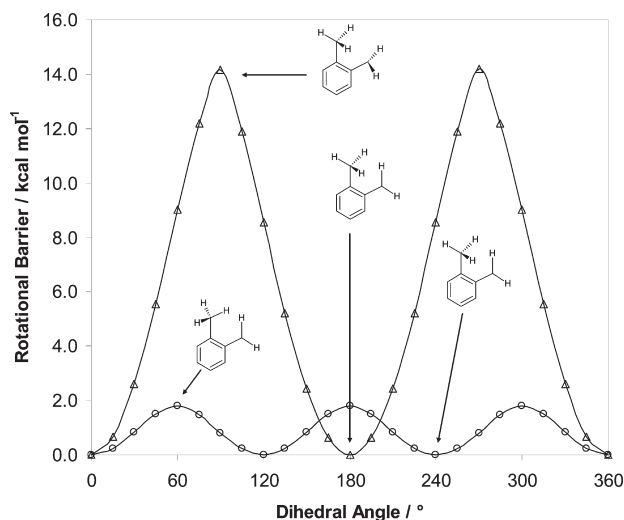
Figure 3. Barrier for internal rotation versus the dihedral angle in 2-methylbenzyl radical (**2**): −CH₃ (○), −CH₂° (△). Points are calculated values at the B3LYP/6-311G(d,p) level of theory.

Figure 5. Barrier for internal rotation versus the dihedral angle in 2-methylbenzylhydroperoxide (**4**): −CH₃ (○), −CH₂OOH (■), −OH (▲), −OOH (◇). Points are calculated values at the B3LYP/6-311G(d,p) level of theory.
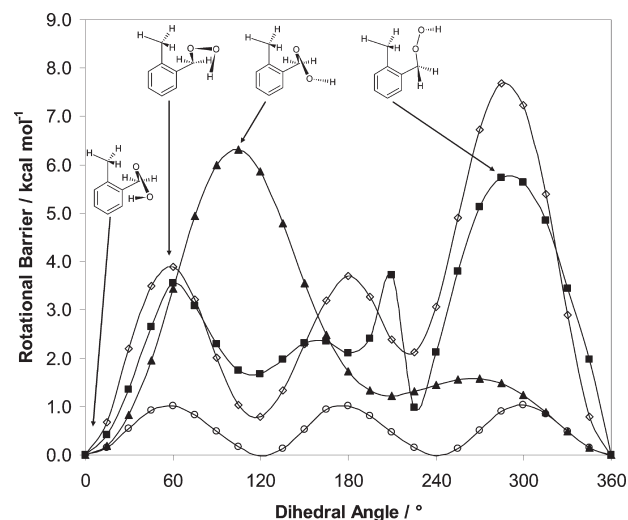
reciprocal square of the uncertainty in enthalpy of formation of the target species. The final $\Delta_f H^\circ(\text{TS})$ value is calculated according to eq 4

$$\Delta_f H^\circ(\text{TS}) = \frac{\displaystyle\sum_{i=1}^{5}\sum_{j=1}^{5} \frac{\Delta_f H^\circ_{i,j}(\text{TS})}{u^2(\text{TS})_{i,j}}}{\displaystyle\sum_{i=1}^{5}\sum_{j=1}^{5} \frac{1}{u^2(\text{TS})_{i,j}}} \tag{4}$$

where $\Delta_f H^\circ_{i,j}(\text{TS})$ is the enthalpy of formation at 298 K of target species TS calculated using the isodesmic reaction i and the calculation method j and $u(\text{TS})_{i,j}$ is its uncertainty. This procedure discriminates against the isodesmic reactions which involve less well-known enthalpies of formation for reference species. As $u(\text{TS})_{i,j}$ is identical for each calculation method (see eq 6), eq 4

can be simplified as shown by eq 5

$$\Delta_f H^\circ(\text{TS}) = \frac{\displaystyle\sum_{i=1}^{5} \frac{1}{u^2(\text{TS})_{i,j}} \sum_{j=1}^{5} \Delta_f H^\circ_{i,j}(\text{TS})}{5 \displaystyle\sum_{i=1}^{5} \frac{1}{u^2(\text{TS})_{i,j}}} \tag{5}$$

Let us consider a target species involved in the isodesmic reaction i whose equation is

$$\text{TS} + \text{RS}_{1,i} = \text{RS}_{2,i} + \text{RS}_{3,i}$$
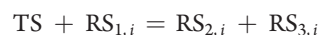
where $\text{RS}_{1,i}$, $\text{RS}_{2,i}$, and $\text{RS}_{3,i}$ are reference species. Then, $\Delta_f H^\circ_{i,j}(\text{TS})$ is expressed as an algebraic sum of enthalpies of formation of the reference species and the standard enthalpy of the isodesmic reaction i $\Delta_r H^\circ_i$ at 298 K evaluated with the calculation method j

596

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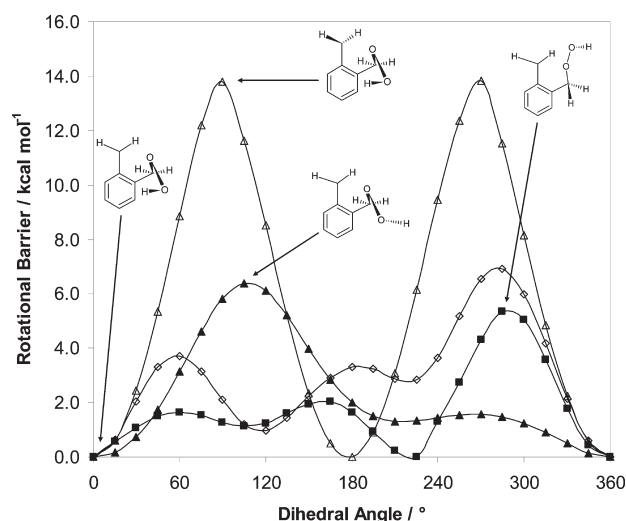
Figure 6. Barrier for internal rotation versus the dihedral angle in 2-(hydroperoxymethyl)benzyl radical (**5**): $-CH_2^\circ$ ($\triangle$), $-CH_2OOH$ ($\blacksquare$), $-OH$ ($\blacktriangle$), $-OOH$ ($\diamond$). Points are calculated values at the B3LYP/6-311G(d,p) level of theory.

Figure 8. Barrier for internal rotation versus the dihedral angle in 1-ethyl-2-methylbenzene (**7**): $-CH_3$ in position 2 ($\circ$), $-CH_3$ in the ethyl group ($\bullet$), $-CH_2CH_3$ ($\ast$). Points are calculated values at the B3LYP/6-311G(d,p) level of theory.

Figure 7. Barrier for internal rotation versus the dihedral angle in 2-(hydroperoxymethyl)benzaldehyde (**6**): $-CHO$ ($\blacklozenge$), $-CH_2OOH$ ($\blacksquare$), $-OH$ ($\blacktriangle$), $-OOH$ ($\diamond$). Points are calculated values at the B3LYP/6-311G(d,p) level of theory.
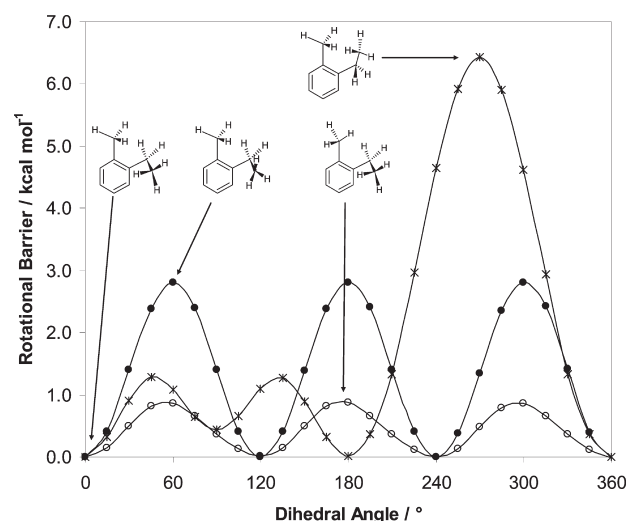

Figure 9. Barrier for internal rotation versus the dihedral angle in 2,3-dimethylphenol (**8**): $-CH_3$ in position 2 ($\circ$), $-CH_3$ in position 3 ($\bullet$), $-OH$ ($\blacktriangle$). Points are calculated values at the B3LYP/6-311G(d,p) level of theory.

as follows

$$\Delta_f H^\circ_{i,j}(TS) = -\Delta_r H^\circ_i - \Delta_f H^\circ(RS_1) + \Delta_f H^\circ(RS_2) + \Delta_f H^\circ(RS_3)$$
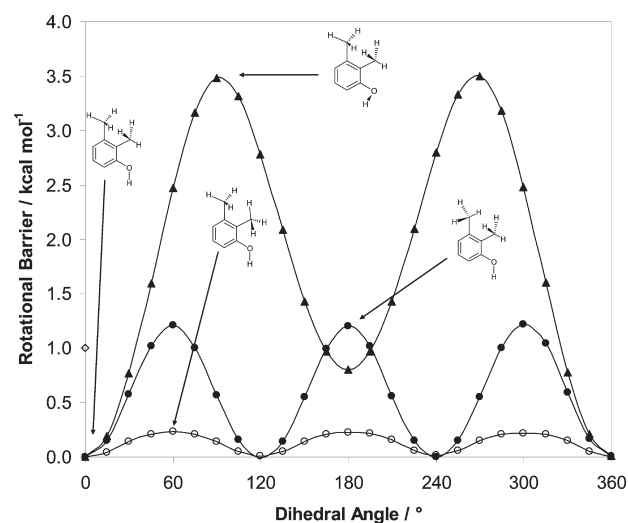
If we consider that $\Delta_f H^\circ(298\text{ K})$ of the reference species and $\Delta_r H^\circ_i$ are independent measurements and have random uncertainties, the uncertainty in $\Delta_f H^\circ_{i,j}(TS)$ is the square root of the quadratic sum of their uncertainties as shown by eq 6[59]

$$u(TS)_{i,j} = \sqrt{\sum_{k=1}^{3} u^2(RS_{k,i}) + u^2(\Delta_r H^\circ_i)} \qquad (6)$$

where $u(RS_{k,i})$ is the uncertainty in $\Delta_f H^\circ(298\text{ K})$ for reference species $RS_{k,i}$ and $u(\Delta_r H^\circ_i)$ is the uncertainty in $\Delta_r H^\circ_i$.

The values of $u(RS_{k,i})$ are withdrawn from the literature. The values of $\Delta_r H^\circ_i$ calculated with each calculation method can be considered as the measurements of the same quantity, the true enthalpy of reaction i. Hence, they are subjected to statistical analysis.[59] With a small number of measurements, the accurate determination of the confidence limits requires the use of Student's t distribution.[59,60] Therefore, the value of $u(\Delta_r H^\circ_i)$ is calculated at a confidence level of 95% as the product of the t value by the sample standard deviation s of the $\Delta_r H^\circ$ values determined by the five different calculation methods, through eq 7

$$u(\Delta_r H^\circ_i) = t\,s = t\sqrt{\frac{\sum_{j=1}^{5}\left(\overline{\Delta_r H^\circ_i} - \Delta_r H^\circ_{i,j}\right)^2}{5-1}} \qquad (7)$$
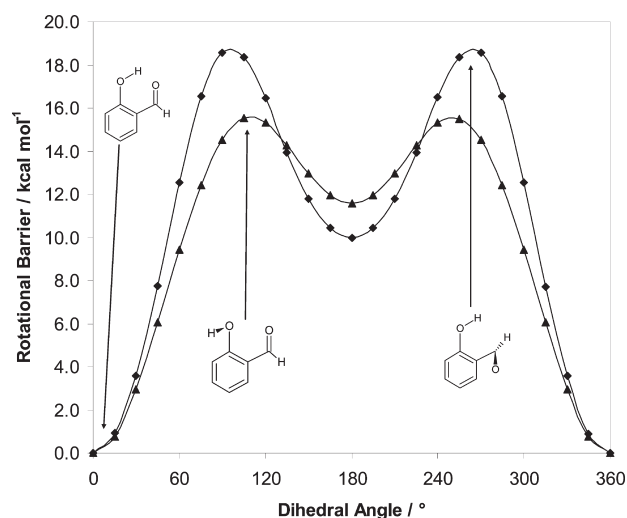
Figure 10. Barrier for internal rotation versus the dihedral angle in 2-hydroxybenzaldehyde (**9**): −OH (▲), −CHO (◆). Points are calculated values at the B3LYP/6-311G(d,p) level of theory.
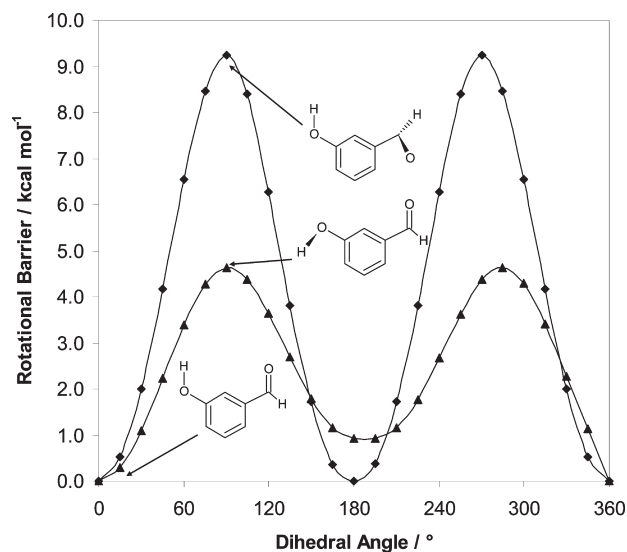
Figure 11. Barrier for internal rotation versus the dihedral angle in 3-hydroxybenzaldehyde (**10**): −OH (▲), −CHO (◆). Points are calculated values at the B3LYP/6-311G(d,p) level of theory.

where t is the coefficient of Student's t distribution at a confidence level of 95% with four degrees of freedom (sample size minus 1) and $\overline{\Delta_r H^\circ_i}$ is the arithmetic average of the $\Delta_r H^\circ$ values across the five calculation methods and $\Delta_r H^\circ_{i,j}$ is the enthalpy of reaction i calculated using the calculation method j. The t value is equal to 2.776 at a confidence level of 95% with four degrees of freedom for a two-tailed t test.[60]

2.2. S°(298 K) and $C_p^\circ(T)$ Calculation. S°(298 K) and $C_p^\circ(T)$ (300 K $\leq T \leq$ 1500 K) were calculated using molecular properties determined at B3LYP/6-311G(d,p) level of theory and statistical thermodynamics through evaluation of translational, rotational, vibrational, and electronic partition functions. The contribution of internal rotors such as −CH$_3$, −CH$_2^\circ$, −CH$_2$OO$^\circ$, −OO$^\circ$, −CH$_2$OOH, −OH, −OOH, −CHO, and −CH$_2$CH$_3$ was determined in two different ways depending on the temperature.

S°(298 K) and C_p°(300 K) were calculated using the rigid-rotor-harmonic-oscillator model. $C_p^\circ(T)$ values at $T \geq$ 400 K were calculated by treating separately internal rotation contributions and translational, external rotational, vibrational, and electronic contributions. In this case, the vibrational frequencies corresponding to internal rotations were excluded in the calculation of vibrational contribution. The contribution to $C_p^\circ(T)$ from an internal rotation was determined with the HR-public program,[61] whose integration algorithm extracts, on a quantum mechanical basis, the partition functions of the internal rotations. The profile of rotational potential as a function of the dihedral angle for an internal rotation was determined at the B3LYP/6-311G(d,p) level of theory. Twenty-four optimized conformations were obtained by scanning the dihedral angle from 0° to 360° at 15° intervals and allowing the remaining molecular structural parameters to be optimized. The scan of the rotational potential V_m as function of the dihedral angle ϕ_m for an internal rotation m is expanded by the HR-public program in a six-term Fourier series given by eq 8

$$V_m(\phi_m) = \sum_{k=1}^{6} \frac{1}{2}V_{mk}(1 - \cos(k\phi_m)) \tag{8}$$

The energy eigenvalues $E_k(m)$ of each internal rotation m are obtained using an efficient computational algorithm which solves the Schrödinger equation on a discretized angular grid (typically about 4000 grid points). Then, the total internal rotation partition function $Q_{rot,int}$ is calculated by the product over the m individual internal rotation partition functions $q_{rot,int,m}$ given by eq 9

$$q_{rot,int,m} = \frac{1}{\sigma_{int}} \sum_{k=1}^{6} g_k(m)\exp\left(-\frac{E_k(m)}{k_B T}\right) \tag{9}$$

where $g_k(m)$ is the degeneracy of the rotational energy level $E_k(m)$ for the mth internal rotation and σ_{int} is the symmetry number of the internal rotation m.

3. RESULTS AND DISCUSSION

3.1. Geometries and Vibrational Frequencies. Optimized structures at B3LYP/6-311G(d,p) level of theory and optimized Cartesian coordinates obtained at CBS-QB3, G3B3, G3MP3, G3, and G4 levels of theory for the ten target species are gathered in Tables 1S−10S in the Supporting Information. Overall, the geometries of the ten species are unchanged, whatever the level of theory.

The unscaled vibrational frequencies obtained at B3LYP/6-311G(d,p) level of theory are given in Table 11S in the Supporting Information. The vibrational frequencies corresponding to internal rotations are marked in bold in Table 11S. For example, the 135 and 164 cm^{-1} vibrational frequencies of o-xylene were attributed to internal rotations about the C$_6$H$_5$−CH$_3$ bonds.

3.2. Rotational Barriers. The target species contain at least two internal rotors and exhibit several different rotational conformers. Internal rotor analysis has been carried out to determine the contribution from each internal rotation to C_p°. The internal rotational barriers for −CH$_3$, −CH$_2^\circ$, −OO$^\circ$, −CH$_2$OO$^\circ$, −OOH, −CH$_2$OOH, −OH, −CHO, −C$_2$H$_5$ groups are listed in Tables 12S−20S. Figures 2−11 show the rotational potential profiles for each internal rotation in the ten target species. They have been determined from relaxed scans of the corresponding dihedral angle at the B3LYP/6-311G(d,p) level of theory. The rotational barrier is expressed as the difference between the total

Table 2. Isodesmic Reactions[a] Used To Calculate $\Delta_f H°$(298 K) of Target Species

reaction number	reaction
	o-Xylene (**1**)
1.1	*o*-xylene + benzene → toluene + toluene
1.2	*o*-xylene + phenol → 2-methylphenol + toluene
1.3	*o*-xylene + phenol → 2,4-dimethylphenol + benzene
1.4	*o*-xylene + phenol → 2,5-dimethylphenol + benzene
1.5	*o*-xylene + phenol → 2,6-dimethylphenol + benzene
	2-Methylbenzyl Radical (**2**)
2.1	2-methylbenzyl rad. + methane → *o*-xylene + methyl rad.
2.2	2-methylbenzyl rad. + ethane → *o*-xylene + ethyl rad.
2.3	2-methylbenzyl rad. + propane → *o*-xylene + *n*-propyl rad.
2.4	2-methylbenzyl rad. + propane → *o*-xylene + *i*-propyl rad.
2.5	2-methylbenzyl rad. + toluene → *o*-xylene + benzyl rad.
	2-Methylbenzylperoxy Radical (**3**)
3.1	2-methylbenzylperoxy rad. + methane → *o*-xylene + methylperoxy rad.
3.2	2-methylbenzylperoxy rad. + ethane → *o*-xylene + ethylperoxy rad.
3.3	2-methylbenzylperoxy rad. + propane → *o*-xylene + *n*-propylperoxy rad.
3.4	2-methylbenzylperoxy rad. + methyl rad. → 2-methylbenzyl rad. + methylperoxy rad.
3.5	2-methylbenzylperoxy rad. + ethyl rad. → 2-methylbenzyl rad. + ethylperoxy rad.
	2-Methylbenzylhydroperoxide (**4**)
4.1	2-methylbenzylhydroperoxide + propane → *o*-xylene + *i*-propylhydroperoxide
4.2	2-methylbenzylhydroperoxide + propane → *o*-xylene + *n*-propylhydroperoxide
4.3	2-methylbenzylhydroperoxide + methylperoxy rad. → 2-methybenzylperoxy rad. + methylhydroperoxide
4.4	2-methylbenzylhydroperoxide + methane → *o*-xylene + methylhydroperoxide
4.5	2-methylbenzylhydroperoxide + ethane → *o*-xylene + ethylhydroperoxide
	2-(Hydroperoxymethyl)benzyl Radical (**5**)
5.1	2-(hydroperoxymethyl)benzyl rad. + methane → 2-methylbenzylhydroperoxide + methyl rad.
5.2	2-(hydroperoxymethyl)benzyl rad. + methane → 2-methylbenzyl rad. + methylhydroperoxide
5.3	2-(hydroperoxymethyl)benzyl rad. + ethane → 2-methylbenzylhydroperoxide + ethyl rad.
5.4	2-(hydroperoxymethyl)benzyl rad. + ethane → 2-methylbenzyl rad. + ethylhydroperoxide
5.5	2-(hydroperoxymethyl)benzyl rad. + propane → 2-methylbenzylhydroperoxide + *n*-propyl rad.
	2-(Hydroperoxymethyl)benzaldehyde (**6**)
6.1	2-(hydroperoxymethyl)benzaldehyde + methane → benzaldehyde + ethylhydroperoxide
6.2	2-(hydroperoxymethyl)benzaldehyde + ethane → benzaldehyde + *i*-propylhydroperoxide
6.3	2-(hydroperoxymethyl)benzaldehyde + ethane → benzaldehyde + *n*-propylhydroperoxide
6.4	2-(hydroperoxymethyl)benzaldehyde + toluene → benzaldehyde + 2-methylbenzylhydroperoxide
6.5	2-(hydroperoxymethyl)benzaldehyde + ethane → ethanal + 2-methylbenzylhydroperoxide
	1-Ethyl-2-methylbenzene (**7**)
7.1	1-ethyl-2-methylbenzene + toluene → ethylbenzene + *o*-xylene
7.2	1-ethyl-2-methylbenzene + methane → *o*-xylene + ethane
7.3	1-ethyl-2-methylbenzene + benzene → ethylbenzene + toluene

Table 2. Continued

reaction number	reaction
7.4	1-ethyl-2-methylbenzene + phenol → ethylbenzene + 3-methylphenol
7.5	1-ethyl-2-methylbenzene + phenol → ethylbenzene + 4-methylphenol
	2,3-Dimethylphenol (8)
8.1	2,3-dimethylphenol + toluene → *o*-xylene + 3-methylphenol
8.2	2,3-dimethylphenol + toluene → *o*-xylene + 4-methylphenol
8.3	2,3-dimethylphenol + benzene → toluene + 3-methylphenol
8.4	2,3-dimethylphenol + benzene → toluene + 4-methylphenol
8.5	2,3-dimethylphenol + phenol → 3-methylphenol + 4-methylphenol
	2-Hydroxybenzaldehyde (9)
9.1	2-hydroxybenzaldehyde + benzene → phenol + benzaldehyde
9.2	2-hydroxybenzaldehyde + toluene → 3-methylphenol + benzaldehyde
9.3	2-hydroxybenzaldehyde + toluene → 4-methylphenol + benzaldehyde
9.4	2-hydroxybenzaldehyde + *o*-xylene → 2,4-dimethylphenol + benzaldehyde
9.5	2-hydroxybenzaldehyde + *o*-xylene → 2,5-dimethylphenol + benzaldehyde
	3-Hydroxybenzaldehyde (10)
10.1	3-hydroxybenzaldehyde + benzene → phenol + benzaldehyde
10.2	3-hydroxybenzaldehyde + toluene → 3-methylphenol + benzaldehyde
10.3	3-hydroxybenzaldehyde + toluene → 4-methylphenol + benzaldehyde
10.4	3-hydroxybenzaldehyde + *o*-xylene → 2,4-dimethylphenol + benzaldehyde
10.5	3-hydroxybenzaldehyde + *o*-xylene → 2,5-dimethylphenol + benzaldehyde

[a] The abbreviation rad. in the equations stands for radical.

electronic energy at 0 K (expressed in kcal mol^{-1}) of each rotational conformer and that of the lowest energy rotational conformer. The maximal barrier is evaluated as the rotational barrier of the highest point on the curve.

Phenyl−Methyl Rotations. The internal rotation around the C_6H_5−CH_3 bond has a 3-fold symmetry and exhibits a maximal rotational barrier of 1.22, 1.80, 0.98, 1.03, 0.87, and 0.23 kcal mol^{-1} for species **1**, **2**, **3**, **4**, **7**, and **8**, respectively (see Figures 2, 3, 4, 5, 8, 9).

Phenyl−Methylene Rotations. The internal rotation around the C_6H_5−$CH_2°$ bond has a 2-fold symmetry, as the −$CH_2°$ fragment is planar, and it exhibits a maximal rotational barrier of 14.19 and 13.83 kcal mol^{-1} for species **2** and **5**, respectively (see Figures 3 and 6). This high rotational barrier can be due to the delocalization of the unpaired electron of −$CH_2°$ group in the conjugated benzenic ring.

Benzyl−OO° and Phenyl−$CH_2OO°$ Rotations. The rotational potential profiles for internal rotation around the $C_6H_5CH_2$−$OO°$ and C_6H_5−$CH_2OO°$ bonds in 2-methylbenzylperoxy radical (**3**) are dissymmetric and show three maxima (see Figure 4). The maximal barriers for internal rotation around the $C_6H_5CH_2$−$OO°$ and C_6H_5−$CH_2OO°$ bonds are equal to 2.80 and 5.23 kcal mol^{-1}, respectively. The first value is in agreement with that determined by da Silva et al.[62] (3.1 kcal mol^{-1}) for benzylperoxy radical at B3LYP/6-31G(d) level of theory, whereas the second is about 4 kcal mol^{-1} higher than that obtained by da Silva et al. (1.5 kcal mol^{-1}). The higher value of the maximal barrier

located at 285° is due to the steric interaction with the methyl group in the ortho position, which does not occur in the case of benzylperoxy radical. If we consider the lower barriers observed at 75° and 135° for methylbenzylperoxy radical, their heights (1.62 and 1.63 kcal mol^{-1}, respectively) agree well with the barrier of 1.5 kcal mol^{-1} for benzylperoxy radical.

Benzyl−OOH and Phenyl−CH_2OOH Rotations. The internal rotation about the $C_6H_5CH_2$−OOH bond presents a maximal rotational barrier of 7.69, 6.92, and 6.65 kcal mol^{-1} for species **4**, **5**, and **6**, respectively (see Figures 5, 6, and 7). The analogous maximal rotational barrier in the case of vinyl, allyl, and phenyl hydroperoxides varies from 3.55 to 6.49 kcal mol^{-1} at the same level of theory.[52] The internal rotation about the C_6H_5−CH_2OOH bond exhibits a maximal barrier of 5.72, 5.34, and 3.60 kcal mol^{-1} for species **4**, **5**, and **6**, respectively (see Figures 5, 6, and 7). The rotational potential profiles show three maxima for species **5** and **6** but four for species **4**.

BenzylO−OH Rotations. The internal rotation about the $C_6H_5CH_2O$−OH bond presents a maximal rotational barrier of 6.32, 6.37, and 3.67 kcal mol^{-1} for species **4**, **5**, and **6**, respectively (see Figures 5, 6, and 7). The analogous maximal barrier in the case of vinyl, allyl, and phenyl hydroperoxides ranges from 5.76 to 8.23 kcal mol^{-1} at the same level of theory.[52] The rotational potential profiles show two maxima for the three species as in the case of vinyl, allyl, and phenyl hydroperoxides. However, the lower maximum of species **4**, **5**, and **6** is higher than that of vinyl,

Table 3. $\Delta_f H°$(298 K) of Reference Species Used in Isodesmic Reactions with Its Uncertainty

species	$\Delta_f H°$(298 K), kcal mol^{-1}	reference
methane	-17.89 ± 0.08	Prosen et al.[64]
ethane	-20.04 ± 0.07	Pittam et al.[65]
propane	-25.02 ± 0.12	Pittam et al.[65]
benzene	19.82 ± 0.12	Prosen et al.[66]
toluene	11.95 ± 0.15	Prosen et al.[66]
ethylbenzene	7.12 ± 0.20	Prosen et al.[66]
ethanal	-39.53 ± 0.07	Burcat and Ruscic[70]
phenol	-23.03 ± 0.14	Cox et al.[67]
2-methylphenol	-30.67 ± 0.21	Cox et al.[67]
3-methylphenol	-31.94 ± 0.26	Cox et al.[67]
4-methylphenol	-29.94 ± 0.36	Cox et al.[67]
2,4-dimethylphenol	-38.95 ± 0.18	Andon et al.[68]
2,5-dimethylphenol	-38.65 ± 0.12	Andon et al.[68]
2,6-dimethylphenol	-38.68 ± 0.13	Andon et al.[68]
benzaldehyde	-8.80 ± 0.72	Ambrose et al.[69]
methyl radical	35.06 ± 0.07	Burcat and Ruscic[70]
ethyl radical	28.61 ± 0.17	Burcat and Ruscic[70]
n-propyl radical	24.21 ± 0.24	Burcat and Ruscic[70]
i-propyl radical	21.56 ± 0.48	Burcat and Ruscic[70]
benzyl radical	49.71 ± 0.41	Ruscic et al.[71]
methylperoxy radical	2.92 ± 0.22	Simmie et al.[72]
ethylperoxy radical	-5.62 ± 0.17	Simmie et al.[72]
n-propylperoxy radical	-10.54 ± 0.26	Simmie et al.[72]
methylhydroperoxide	-30.95 ± 0.22	Simmie et al.[72]
ethylhydroperoxide	-39.13 ± 0.22	Simmie et al.[72]
n-propylhydroperoxide	-43.83 ± 0.26	Simmie et al.[72]
i-propylhydroperoxide	-47.90 ± 0.22	Simmie et al.[72]
o-xylene	4.57 ± 0.07	this work
2-methylbenzyl radical	42.50 ± 0.24	this work
2-methylbenzylperoxy radical	20.07 ± 0.37	this work
2-methylbenzylhydroperoxide	-14.07 ± 0.12	this work

allyl, and phenyl hydroperoxides, which is always below 1 kcal mol^{-1}.

Phenyl−OH Rotations. For the species **4**, **5**, **6**, **8**, **9**, and **10**, the maximal barriers for internal rotation around the C_6H_5−OH bond are calculated to be 6.32, 6.37, 3.67, 3.50, 15.52, and 4.64 kcal mol^{-1}, respectively (see Figures 5, 6, 7, 9, 10, and 11). In the case of 2-hydroxybenzaldehyde (**9**), the maximal barrier for internal rotation around the C_6H_5−OH bond is significantly higher than those of other species: this is due to a hydrogen bond between the O atom of the CHO function and the H atom of the OH function. In fact, the O···H interatomic distance is 1.75 Å, which is significantly less than the sum of the van der Waals radii[63] of H and O atoms (1.20 + 1.50 = 2.70 Å).

Phenyl−CHO Rotations. For the species **6**, **9**, and **10** the maximal barriers for internal rotation around the C_6H_5−CHO bond are equal to 8.92, 18.56, and 9.24 kcal mol^{-1}, respectively (see Figures 7, 10, and 11). Again, the significantly higher maximal barrier in the case of 2-hydroxybenzaldehyde (**9**) is explained by the hydrogen bond between the O atom of the CHO function and the H atom of the OH function. In the case of 3-hydroxybenzaldehyde (**10**), the rotational potential profile exhibits a 2-fold symmetry.

3.3. $\Delta_f H°$(298 K) Values. For each target species, five isodesmic reactions, which are reported in Table 2, were used to determine its $\Delta_f H°$(298 K). $\Delta_f H°$(298 K) of the reference species involved in these reactions are listed in Table 3 with their uncertainty and the references[64−73] from which they have been taken. $\Delta_r H°$(298 K) of isodesmic reactions and their uncertainty $u(\Delta_r H)$, as well as $\Delta_f H°$(298 K) of the target species for the five calculation methods (CBS-QB3, G3B3, G3MP2, G3, and G4) are listed in Table 4 in kcal mol^{-1}. Overall, $\Delta_f H°$(298 K) values among the five calculation methods and the sets of five isodesmic reactions appear very consistent.

Concerning $\Delta_f H°$(298 K) of *o*-xylene (**1**), the experimental values of Prosen et al.[66] (4.54 ± 0.26 kcal mol^{-1}) and Chirico et al.[74] (4.57 ± 0.05 kcal mol^{-1}), those obtained using additivity methods by Battin-Leclerc et al.[30] (4.5 kcal mol^{-1}) and Santos et al.[28] (4.52 kcal mol^{-1}), and the atomization G3(MP2)// B3LYP value of Taskinen[29] (4.47 kcal mol^{-1}) are in very good agreement with our value (4.57 ± 0.07 kcal mol^{-1}). The atomization G3X and G3SX values (3.96 and 4.05 kcal mol^{-1}) calculated by da Silva et al.[27] are about 0.6 kcal mol^{-1} lower than ours, whereas the value obtained with a GAM by Orlov et al.[36] (4.83 kcal mol^{-1}) is about 0.3 kcal mol^{-1} higher.

Regarding $\Delta_f H°$(298 K) of 2-methybenzyl radical (**2**), the values obtained with a GAM by Battin-Leclerc et al.[30] (42.0 kcal mol^{-1}) and the atomization G3SX value from da Silva et al.[27] (42.75 kcal mol^{-1}) are in good agreement with our value (42.50 ± 0.24 kcal mol^{-1}). Compared to our value, that determined by Orlov et al.[36] (40.42 kcal mol^{-1}) is about 2 kcal mol^{-1} lower, whereas those calculated by da Silva et al.[27] using the G3X method (43.25 and 43.83 kcal mol^{-1}) are about 1 kcal mol^{-1} higher.

For 2-methylbenzylhydroperoxide (**4**), our $\Delta_f H°$(298 K) value (-14.07 ± 0.12 kcal mol^{-1}) is about 1.5 kcal mol^{-1} higher than the GAM value from Battin-Leclerc et al.[30] (-15.6 kcal mol^{-1}).

For 1-ethyl-2-methylbenzene (**7**), our $\Delta_f H°$(298 K) value (-0.07 ± 0.06 kcal mol^{-1}) is in very good agreement with the GAM value (-0.1 kcal mol^{-1}) determined by Battin-Leclerc et al.[30] Other literature values (0.08,[36] 0.29,[66] -0.26[28] kcal mol^{-1}) lie in the interval $[-0.3 ; 0.3]$ in kcal mol^{-1} in agreement with our recommended value.

Our $\Delta_f H°$(298 K) value for 2,3-dimethylphenol (**8**) (-38.66 ± 0.08 kcal mol^{-1}) is about 1 kcal mol^{-1} lower than literature values (-37.6,[30] -37.60 ± 0.26[68] kcal mol^{-1}). Concerning $\Delta_f H°$(298 K) of 2-hydroxybenzaldehyde (**9**), our value (-58.20 ± 0.16 kcal mol^{-1}) is in good agreement with the experimental value (-58.70 ± 0.53 kcal mol^{-1}) of Ribeiro da Silva et al.[75] and about 1 to 2 kcal mol^{-1} lower than other literature data (-57.7,[38] -56.96 ± 0.60[73] kcal mol^{-1}). Our $\Delta_f H°$(298 K) value for 3-hydroxybenzaldehyde (**10**) (-52.33 ± 0.16 kcal mol^{-1}) agrees well with the isodesmic G3(MP2)//B3LYP/6-31G(d) value (-52.01 kcal mol^{-1}) from Gomez et al.[38]

The accuracy in $\Delta_f H°$(298 K) for target species is due to the high levels of theory used, the reliability of $\Delta_f H°$(298 K) values for reference species, and an appropriate choice of isodesmic reactions. Except for the particular case of 1-ethyl-2-methylbenzene (**7**) which has a $\Delta_f H°$(298 K) close to zero, the relative uncertainty in $\Delta_f H°$(298 K) of target species lie in the range 0.2−1.8% (see Table 4). Many isodesmic reactions have a $\Delta_r H°$ value very close to zero which indicates an optimal cancelation of systematic errors in the quantum chemistry calculations. Only eight isodesmic reactions (2.1, 2.2, 2.3, 3.4, 3.5, 5.1, 5.3, 5.5)

Table 4. $\Delta_r H°$ of Isodesmic Reactions and $\Delta_f H°$ of Target Species at 298 K (in kcal mol^{-1}) Determined at Five Levels of Theory

reaction number	CBS-QB3 $\Delta_r H°$	CBS-QB3 $\Delta_f H°$	G3B3 $\Delta_r H°$	G3B3 $\Delta_f H°$	G3MP2 $\Delta_r H°$	G3MP2 $\Delta_f H°$	G3 $\Delta_r H°$	G3 $\Delta_f H°$	G4 $\Delta_r H°$	G4 $\Delta_f H°$	$u(\Delta_r H°)$[a]
					o-Xylene (**1**)						
1.1	0.46	3.62	0.19	3.89	0.18	3.90	0.12	3.96	0.14	3.94	0.38
1.2	−0.49	4.80	−0.52	4.83	−0.49	4.80	−0.56	4.87	−0.59	4.90	0.12
1.3	−0.31	4.21	−0.11	4.01	−0.02	3.92	−0.13	4.03	−0.05	3.95	0.32
1.4	−0.51	4.71	−0.50	4.70	−0.38	4.58	−0.50	4.70	−0.42	4.62	0.16
1.5	−1.16	5.33	−0.90	5.07	−0.83	5.00	−0.91	5.08	−0.85	5.02	0.37
final[b] $\Delta_f H°$	4.57 ± 0.07 (1.5%[c])										
literature	3.96,[27] 4.05,[27] 4.52,[28] 4.47,[29] 4.5,[30] 4.83,[36] 4.54 ± 0.26,[66] 4.57 ± 0.05[74]										
					2-Methylbenzyl Radical (**2**)						
2.1	14.80	42.72	13.14	44.38	12.16	45.36	13.67	43.85	14.97	42.55	3.25
2.2	11.09	42.13	9.85	43.37	9.11	44.11	10.59	42.63	11.15	42.07	2.42
2.3	11.39	42.41	10.16	43.64	9.44	44.36	10.91	42.89	11.18	42.62	2.23
2.4	8.36	42.79	7.51	43.64	6.90	44.25	8.35	42.80	8.35	42.80	1.84
2.5	−0.03	42.36	−0.05	42.38	−0.06	42.39	−0.06	42.39	0.28	42.05	0.41
final[b] $\Delta_f H°$	42.50 ± 0.24 (0.6%[c])										
literature	43.25,[27] 42.75,[27] 43.83,[27] 42.0,[30] 40.42[36]										
					2-Methylbenzylperoxy Radical (**3**)						
3.1	4.79	20.59	4.96	20.42	4.71	20.67	5.03	20.35	6.37	19.01	1.90
3.2	−1.49	20.48	−1.32	20.31	−1.56	20.55	−1.35	20.34	−0.10	19.09	1.68
3.3	−1.64	20.69	−1.50	20.55	−1.69	20.74	−1.55	20.60	−0.46	19.51	1.43
3.4	−10.00	20.36	−8.18	18.54	−7.45	17.81	−8.64	19.00	−8.59	18.95	2.59
3.5	−12.58	20.85	−11.17	19.44	−10.67	18.94	−11.94	20.21	−11.25	19.52	2.07
final[b] $\Delta_f H°$	20.07 ± 0.37 (1.8%[c])										
					2-Methylbenxylhydroperoxide (**4**)						
4.1	−4.52	−13.79	−4.32	−13.99	−4.57	−13.74	−4.45	−13.86	−4.62	−13.69	0.33
4.2	−0.04	−14.20	0.19	−14.43	−0.09	−14.15	0.10	−14.34	−0.20	−14.04	0.43
4.3	0.84	−14.64	0.97	−14.77	0.84	−14.64	0.91	−14.71	−1.00	−12.80	2.35
4.4	5.63	−14.12	5.93	−14.42	5.55	−14.04	5.94	−14.43	5.37	−13.86	0.69
4.5	−0.23	−14.29	0.02	−14.54	−0.31	−14.21	−0.04	−14.48	−0.47	−14.05	0.55
final[b] $\Delta_f H°$	−14.07 ± 0.12 (0.9%[c])										
literature	−15.6[30]										
					2-(Hydroperoxymethyl)benzyl Radical (**5**)						
5.1	14.53	24.35	12.61	26.27	11.64	27.24	13.18	25.70	15.12	23.76	3.92
5.2	5.36	24.08	5.41	24.03	5.03	24.41	5.45	23.99	5.53	23.91	0.53
5.3	10.82	23.76	9.32	25.26	8.59	25.99	10.10	24.48	11.31	23.27	3.05
5.4	−0.50	23.91	−0.51	23.92	−0.83	24.24	−0.53	23.94	−0.31	23.72	0.51
5.5	11.12	24.04	9.64	25.52	8.93	26.23	10.42	24.74	11.33	23.83	2.80
final[b] $\Delta_f H°$	24.06 ± 0.19 (0.8%[c])										
					2-(Hydroperoxymethyl)benzaldehyde (**6**)						
6.1	4.26	−34.30	4.38	−34.42	4.06	−34.10	4.56	−34.60	4.04	−34.08	0.61
6.2	−2.74	−33.92	−2.67	−33.99	−2.92	−33.74	−2.55	−34.11	−2.91	−33.75	0.44
6.3	1.74	−34.33	1.83	−34.42	1.56	−34.15	2.00	−34.59	1.51	−34.10	0.56
6.4	−1.52	−33.30	−1.51	−33.31	−1.38	−33.44	−1.29	−33.53	−1.52	−33.30	0.28
6.5	0.37	−33.93	0.38	−33.94	0.32	−33.88	0.68	−34.24	−0.10	−33.46	0.77
final[b] $\Delta_f H°$	−33.91 ± 0.17 (0.5%[c])										
					1-Ethyl-2-methylbenzene (**7**)						
7.1	−0.66	0.40	−0.65	0.39	−0.58	0.32	−0.60	0.34	−0.66	0.40	0.10
7.2	2.38	0.04	2.43	−0.01	2.46	−0.04	2.52	−0.10	2.53	−0.11	0.18
7.3	−0.20	−0.55	−0.46	−0.29	−0.40	−0.35	−0.48	−0.27	−0.52	−0.23	0.35

Table 4. Continued

reaction number	CBS-QB3		G3B3		G3MP2		G3		G4		$u(\Delta_r H°)^a$
	$\Delta_r H°$	$\Delta_f H°$	$\Delta_r H°$	$\Delta_f H°$	$\Delta_r H°$	$\Delta_f H°$	$\Delta_r H°$	$\Delta_f H°$	$\Delta_r H°$	$\Delta_f H°$	
7.4	−0.41	−1.38	−0.59	−1.20	−0.50	−1.29	−0.61	−1.18	−0.63	−1.16	0.26
7.5	0.04	0.17	0.00	0.21	0.07	0.14	−0.03	0.24	−0.06	0.27	0.15
final[b] $\Delta_f H°$	−0.07 ± 0.06 (86%[c])										
literature	−0.26,[28] 0.08,[36] −0.1,[30] 0.29[66]										
	2,3-Dimethylphenol (8)										
8.1	−0.35	−38.97	−0.39	−38.93	−0.35	−38.97	−0.38	−38.94	−0.37	−38.95	0.05
8.2	0.10	−37.42	0.21	−37.53	0.22	−37.54	0.20	−37.52	0.20	−37.52	0.14
8.3	0.11	−39.92	−0.20	−39.61	−0.17	−39.64	−0.26	−39.55	−0.23	−39.58	0.41
8.4	0.56	−38.37	0.40	−38.21	0.40	−38.21	0.32	−38.13	0.34	−38.15	0.25
8.5	0.34	−39.19	0.27	−39.12	0.31	−39.16	0.19	−39.04	0.23	−39.08	0.17
final[b] $\Delta_f H°$	−38.66 ± 0.08 (0.2%[c])										
literature	−37.6,[30] −37.60 ± 0.26[68]										
	2-Hydroxybenzaldehyde (9)										
9.1	6.45	−58.10	6.38	−58.03	6.29	−57.94	6.50	−58.15	6.25	−57.90	0.29
9.2	6.23	−58.92	6.25	−58.94	6.20	−58.89	6.36	−59.05	6.13	−58.82	0.24
9.3	6.68	−57.37	6.85	−57.54	6.77	−57.46	6.95	−57.64	6.70	−57.39	0.31
9.4	6.13	−58.45	6.28	−58.60	6.27	−58.59	6.37	−58.69	6.19	−58.51	0.24
9.5	5.94	−57.96	5.89	−57.91	5.91	−57.93	6.00	−58.02	5.83	−57.85	0.18
final[b] $\Delta_f H°$	−58.20 ± 0.16 (0.3%[c])										
literature	−57.77,[38] −56.96 ± 0.60,[73] −58.70 ± 0.53[75]										
	3-Hydroxybenzaldehyde (10)										
10.1	0.76	−52.41	0.43	−52.08	0.47	−52.12	0.47	−52.12	0.38	−52.03	0.42
10.2	0.55	−53.24	0.29	−52.98	0.37	−53.06	0.34	−53.03	0.26	−52.95	0.31
10.3	1.00	−51.69	0.89	−51.58	0.95	−51.64	0.92	−51.61	0.83	−51.52	0.17
10.4	0.45	−52.77	0.32	−52.64	0.45	−52.77	0.34	−52.66	0.33	−52.65	0.19
10.5	0.25	−52.27	−0.07	−51.95	0.09	−52.11	−0.03	−51.99	−0.04	−51.98	0.37
final[b] $\Delta_f H°$	−52.33 ± 0.16 (0.3%[c])										
literature	−52.01[38]										

[a] Uncertainty in $\Delta_r H°$. [b] Weighted average across the $\Delta_f H°$ values obtained by the five isodesmic reactions and the five levels of theory. [c] Relative uncertainty in final $\Delta_f H°$.

among 50 isodesmic reactions have a $\Delta_r H°$ value higher than 10 kcal mol^{-1} in absolute value. In addition to bond conservation, we have tried to use isodesmic reactions with group conservation and thus to get better cancelation of errors than in the case of a conventional isodesmic reaction.

3.4. $S°(298\ K)$ and $C_p°(300\ K \leq T \leq 1500\ K)$ Values. $S°(298\ K)$ and $C_p°(300\ K \leq T \leq 1500\ K)$ values of the target species are summarized in Table 5. The existence of low-energy rotation conformers and the transition through internal rotation barriers between the conformers has significant effects on $C_p°$ values of species at temperatures higher than 400 K. As a consequence, the total $C_p°(T \geq 400\ K)$ value is calculated as the sum of two terms: the TERVE and IR terms. The TERVE term represents the sum of translational, external rotational, vibrational, and electronic contributions. The IR term includes the contributions from each internal rotation determined with the HR-public program.[61] The internal symmetry number σ_{int} of each internal rotation is mentioned in Table 5; it is used to calculate the internal rotation partition function. The external symmetry number σ_{ext} (equal to the number of unique orientations of the rigid molecule that only interchange identical atoms) of each target species used to calculate the rotational partition function

for $S°(298\ K)$ is also reported in Table 5. If the species has two optical isomers as in the case of hydroperoxides (species **4, 5**, and **6**), a contribution due to the entropy of mixing is included in the total listed in Table 5. The entropy of mixing ΔS_{mix} is given by eq 10

$$\Delta S_{mix} = R \ln n(oi) \qquad (10)$$

where $R = 1.987$ cal K^{-1} mol^{-1} and $n(oi)$ is the number of optical isomers for the species. It is equal to 1.38 cal K^{-1} mol^{-1} for two optical isomers.

Table 5 also lists comparisons with literature data for *o*-xylene (**1**), 2-methylbenzyl radical (**2**), 2-methylbenzylperoxy radical (**3**), and 2,3-dimethylphenol (**8**), and computed values with THERM AG database for *o*-xylene (**1**) and 2-methylbenzyl radical (**2**).

For *o*-xylene (**1**), our $S°(298\ K)$ value is in good agreement with the experimental data of Pitzer et al.,[76] the value taken from TRC Thermodynamic Tables[77] and the value determined with THERM: 83.70, 84.51, 84.57, and 84.77 cal K^{-1} mol^{-1}, respectively. A very good agreement is also observed between our $C_p°(T)$ values, the experimental ones of Pitzer et al.[76] and Draeger et al.,[78] the value from TRC Thermodynamic Tables,[77]

Table 5. $S°(298\ K)$ and $C_p°(T)$ of Target Species (in cal $K^{-1}\ mol^{-1}$) Calculated at B3LYP/6-311G(d,p) Level of Theory

target species and data[a] needed for entropy calculation	contributions[b] to $C_p°(T)$	$S°$ 298 K	$C_p°$ 300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
o-xylene (**1**)	TERVE			38.29	46.89	54.02	64.87	72.59	84.08
$\sigma_{ext} = 2$	IR($-CH_3$) $\sigma_{int} = 3$			1.41	1.29	1.20	1.12	1.08	1.03
	IR($-CH_3$) $\sigma_{int} = 3$			1.41	1.29	1.20	1.12	1.08	1.03
	total	83.70	32.29	41.11	49.47	56.41	67.11	74.74	86.14
	Pitzer et al.[76]	84.51		41.08	49.16	56.01	66.70	74.36	85.98
	Draeger et al.[78]		31.83	41.01	49.23	56.19	66.92	74.62	86.11
	TRC Tables[77]	84.57	31.79	40.74	48.83	55.75	66.52	74.35	86.09
	THERM[c]	84.77	31.79	40.74	48.83	55.75	66.52	74.35	86.09
2-methylbenzyl radical (**2**)	TERVE			38.32	46.29	52.78	62.49	69.36	79.62
$\sigma_{ext} = 1$	IR($-CH_3$) $\sigma_{int} = 3$			1.70	1.53	1.41	1.24	1.17	1.08
	IR($-CH_2$) $\sigma_{int} = 2$			1.79	1.89	1.96	2.03	2.08	2.10
	total	84.37	32.03	41.81	49.71	56.15	65.77	72.61	82.80
	da Silva et al.[27]	83.924	31.143	40.42	48.33	54.80	64.52	71.43	81.90
	THERM[c]	84.97	32.54	41.34	48.96	55.33	65.11	72.17	82.72
2-methylbenzylperoxy radical (**3**)	TERVE			42.61	51.70	59.11	70.08	77.70	88.81
$\sigma_{ext} = 1$	IR($-CH_3$) $\sigma_{int} = 3$			1.27	1.20	1.12	1.08	1.05	1.03
	IR($-CH_2OO$) $\sigma_{int} = 1$			2.20	1.94	1.77	1.55	1.43	1.24
	IR(-OO) $\sigma_{int} = 1$			1.58	1.48	1.39	1.27	1.20	1.10
	total	99.02	37.91	46.66	55.31	63.38	73.97	81.38	92.18
2-methylbenzylhydroperoxide (**4**)	TERVE			43.14	52.53	60.21	71.61	79.59	91.42
$\sigma_{ext} = 2$	IR($-CH_3$) $\sigma_{int} = 3$			1.31	1.22	1.15	1.10	1.05	1.03
$n(oi) = 2$	IR($-CH_2OOH$) $\sigma_{int} = 1$			2.29	1.98	1.79	1.55	1.41	1.24
	IR($-OH$) $\sigma_{int} = 1$			2.32	2.06	1.89	1.70	1.58	1.39
	IR(-OOH) $\sigma_{int} = 1$			2.63	2.53	2.37	2.06	1.82	1.48
	total	99.01[d]	39.77	51.70	60.33	67.40	78.01	85.44	96.56
2-(hydroperoxymethyl)benzyl radical (**5**)	TERVE			42.97	51.79	58.84	69.19	76.34	86.97
$\sigma_{ext} = 1$	IR($-CH_2$) $\sigma_{int} = 2$			1.79	1.89	1.96	2.03	2.10	2.13
$n(oi) = 2$	IR($-CH_2OOH$) $\sigma_{int} = 1$			2.22	1.96	1.77	1.55	1.43	1.24
	IR($-OH$) $\sigma_{int} = 1$			2.22	2.01	1.89	1.70	1.58	1.39
	IR(-OOH) $\sigma_{int} = 1$			3.32	2.99	2.70	2.20	1.89	1.48
	total	99.11[d]	39.56	52.53	60.64	67.16	76.67	83.34	93.21
2-(hydroperoxymethyl)benzaldehyde (**6**)	TERVE			43.36	52.22	59.39	69.93	77.17	87.67
$\sigma_{ext} = 1$	IR($-CHO$) $\sigma_{int} = 1$			2.96	3.01	2.96	2.70	2.39	1.79
$n(oi) = 2$	IR($-CH_2OOH$) $\sigma_{int} = 1$			2.80	2.27	1.91	1.55	1.36	1.17
	IR($-OH$) $\sigma_{int} = 1$			3.08	2.65	2.29	1.79	1.55	1.22
	IR(-OOH) $\sigma_{int} = 1$			4.06	3.92	3.61	2.94	2.44	1.74
	total	98.66[d]	39.89	56.26	64.08	70.17	78.92	85.89	93.59
1-ethyl-2-methylbenzene (**7**)	TERVE			43.00	53.08	61.47	74.28	83.44	97.08
$\sigma_{ext} = 1$	IR($-CH_3$)[e] $\sigma_{int} = 3$			1.22	1.15	1.10	1.05	1.03	1.00
	IR($-CH_3$)[f] $\sigma_{int} = 3$			2.13	1.96	1.82	1.55	1.39	1.20
	IR($-CH_2CH_3$) $\sigma_{int} = 1$			1.70	1.60	1.55	1.51	1.46	1.34
	total	92.30	37.26	48.04	57.79	65.94	78.39	87.31	100.62
2,3-dimethylphenol (**8**)	TERVE			41.66	50.38	57.58	68.43	67.15	87.69
$\sigma_{ext} = 1$	IR($-CH_3$)[g] $\sigma_{int} = 3$			1.00	1.00	1.00	1.00	1.00	1.00
	IR($-CH_3$)[h] $\sigma_{int} = 3$			1.43	1.29	1.22	1.12	1.08	1.03
	IR($-OH$) $\sigma_{int} = 1$			2.46	2.25	2.03	1.72	1.51	1.24
	total	91.80	37.14	46.56	54.92	61.83	72.28	79.73	90.97
	Kudchadker et al.[79]		39.41	49.11	57.46	64.35	74.77	82.17	93.26
	TRC Tables[77]	93.23	39.41	49.11	57.46	64.35	74.77	82.17	
2-hydroxybenzaldehyde (**9**)	TERVE			35.30	42.52	48.33	56.81	62.57	70.84
$\sigma_{ext} = 1$	IR($-OH$) $\sigma_{int} = 1$			1.51	1.70	1.84	2.13	2.44	3.11
	IR($-CHO$) $\sigma_{int} = 1$			1.94	1.98	2.03	2.25	2.53	3.20

Table 5. Continued

target species and data[a] needed for entropy calculation	contributions[b] to $C_p°(T)$	$S°$	$C_p°$						
		298 K	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
	total	83.08	30.26	38.74	46.20	52.20	61.19	67.54	77.15
3-hydroxybenzaldehyde (**10**)	TERVE		36.42	43.40	49.02	57.19	62.79	70.84	
$\sigma_{\text{ext}} = 1$	IR(−OH) $\sigma_{\text{int}} = 2$		2.82	2.65	2.46	2.10	1.82	1.43	
	IR(−CHO) $\sigma_{\text{int}} = 1$		2.06	2.10	2.15	2.20	2.20	2.03	
	total	85.57	31.57	41.30	48.16	53.63	61.50	66.80	74.31

[a] σ_{ext}: external symmetry number, n(oi): number of optical isomers. [b] TERVE: sum of translational, external rotational, vibrational, and electronic contributions, IR: contribution from the internal rotation of the specified rotor, σ_{int}: internal symmetry number of the rotor. [c] Thermochemical properties calculated using THERM group database. [d] Entropy of mixing $R \ln n$(oi) has been added. [e] Methyl in position 2. [f] Methyl of the ethyl substituent. [g] Methyl in position 2. [h] Methyl in position 3.

Table 6. Target Groups Developed in This Work

target group[a]	species containing the group	origin of thermochemical properties	σ_{ext}[b]	σ_{int}[c]	$R \ln 2$[d]
C/CB/H2/OO	benzylhydroperoxide	da Silva et al.[62]	1	1	added
CB/CO	benzaldehyde	Sebbar et al.[81]	2	1	
ORT/CH2OOH/ME	2-methylbenzylhydroperoxide (**4**)	this work	1	3	added
ORT/ET/ME	1-ethyl-2-methylbenzene (**7**)	this work	1	9	
ORT/CHO/OH	2-hydroxybenzaldehyde (**9**)	this work	1	1	
ORT/CHO/CH2OOH	2-(hydroperoxymethyl)benzaldehyde (**6**)	this work	1	1	added
MET/CHO/OH	3-hydroxybenzaldehyde (**10**)	this work	1	1	
ME/ME/OH123	2,3-dimethyphenol (**8**)	this work	1	9	

[a] CB stands for benzenic carbon, ORT stands for two substituents of a benzenic cycle in ortho position, ET stands for an ethyl substituent, MET stands for two substituents of a benzenic cycle in meta position, ME stands for a methyl substituent, the group ME/ME/OH123 takes into account the interaction between two methyl substituents and a hydroxyl substituent of a benzenic cycle located ones besides the others (position numbered 1, 2, 3). [b] External symmetry number of species. [c] Internal symmetry number of species. [d] Entropy of mixing for two optical isomers.

and the values calculated with THERM: for example at 400 K, the values are 41.11, 41.08, 41.01, and 40.74 cal K^{-1} mol^{-1}, respectively.

For 2-methylbenzyl radical (**2**), a very good agreement is observed between our $S°(298 \text{ K})$ value and the one from THERM: 84.37 and 84.97 cal K^{-1} mol^{-1}, respectively. The value calculated by da Silva et al.[27] at B3LYP/6-31G(2df,p) level of theory is about 1 cal K^{-1} mol^{-1} lower than ours. A very good agreement is also observed between our $C_p°(T)$ values and the values from THERM: for example at 400 K, the values are 41.80 and 41.34 cal K^{-1} mol^{-1}, respectively. The $C_p°(T)$ values calculated by da Silva et al.[27] are between 1.0 to 1.5 cal K^{-1} mol^{-1} lower than our value.

For 2,3-dimethylphenol (**8**), our $S°(298 \text{ K})$ value is 1.42 cal K^{-1} mol^{-1} lower than the value reported in TRC Thermodynamic Tables.[77] Our $C_p°(T)$ values are between 2.0 to 2.5 cal K^{-1} mol^{-1} lower than those calculated by Kudchadker et al.:[79] for example, 54.92 and 57.46 cal K^{-1} mol^{-1} for $C_p°(400 \text{ K})$, respectively.

3.5. Additivity Group Values. In this work, $\Delta_f H°(298 \text{ K})$, $S°(298 \text{ K})$, and $C_p°(300 \text{ K} \leq T \leq 1500 \text{ K})$ values have been calculated for eight target groups useful for substituted benzenic species. The target groups are listed in Table 6. Among these eight groups, two groups have been developed using the thermochemical properties of benzenic species taken from the literature: the C/CB/H2/OO and the CB/CO groups (CB stands for a benzenic carbon). The six others groups are non-next-nearest neighbor interaction groups[80] to be used to improve accuracy in calculation of thermochemical properties for two- or three-substituted benzenic species. These interaction groups take into

account the interaction between two substituents in ortho (ORT/CH2OOH/ME, ORT/ET/ME, ORT/CHO/OH, ORT/CHO/CH2OOH) or meta (MET/CHO/OH) positions, and the interaction between three substituents (ME/ME/OH123) located one beside the other (positions numbered 1, 2, 3) on a benzenic cycle. They have been developed using the thermochemical properties of six target species considered in this work. Each target group has been determined from thermochemical properties of only one species.

$\Delta_f H°(298 \text{ K})$, $S°(298 \text{ K})$, and $C_p°(T)$ values for a target group are determined using reference group values listed in Table 7. Most of reference group values are taken from THERM AG database. However, the CO/CB/H and OO/C/H group values have been updated and are reported in Table 8. The new values of CO/CB/H group are those calculated recently by Sebbar et al.[81] in a study on thermochemical properties for oxygenated aromatics. Concerning the OO/C/H group, the new $\Delta_f H°(298 \text{ K})$ value has been taken equal to the recommended value by Simmie et al.[72] from $\Delta_f H°(298 \text{ K})$ of a series of alkylhydroperoxides computed by quantum chemistry methods and an isodesmic reaction procedure. The $S°(298 \text{ K})$ and $C_p°(T)$ values for this group have been deduced from thermochemical properties of methylhydroperoxide recommended by Dorofeeva et al.[82] and the values of C/H3/OO and OI reference groups contained in the decomposition in group of methylhydroperoxide (see Table 7). The OI group is a special group of THERM AG database. For this group, contributions to thermochemical properties are equal to zero with the exception of $S°(298 \text{ K})$ whose value is equal to $R \ln 2$. This group is used to take into account the mixing entropy

605

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Table 7. Reference Group Values Used To Calculate Target Group Values

			cal K^{-1} mol^{-1}						
group	$\Delta_f H°$(298 K), kcal mol^{-1}	$S°$(298 K)	$C_p°$(300 K)	$C_p°$(400 K)	$C_p°$(500 K)	$C_p°$(600 K)	$C_p°$(800 K)	$C_p°$(1000 K)	$C_p°$(1500 K)
C/C/H3[a]	−10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C/C2/H2[a]	−5.00	9.42	5.50	6.95	8.25	9.35	11.07	12.34	14.20
C/CB/H3[a]	−10.20	30.41	6.19	7.84	9.40	10.79	13.02	14.77	17.58
C/C/CB/H2[a]	−4.86	9.34	5.84	7.61	8.98	10.01	11.49	12.54	13.76
CB/C[a]	5.51	−7.69	2.67	3.14	3.68	4.15	4.96	5.44	5.98
CB/H[a]	3.30	11.53	3.24	4.44	5.46	6.30	7.54	8.41	9.73
CB/O[a]	−0.90	−10.20	3.90	5.30	6.20	6.60	6.90	6.90	7.07
C/C/H2/OO[a]	−8.80	10.95	4.78	6.34	7.78	9.03	10.95	12.30	14.13
C/H3/OO[a]	−10.00	30.30	6.19	7.84	9.40	10.79	13.02	14.77	17.58
O/CB/H[a]	−37.90	29.10	4.30	4.50	4.82	5.23	6.02	6.61	7.44
OI[a]	0.00	1.37	0.00	0.00	0.00	0.00	0.00	0.00	0.00
CO/CB/H[b]	−29.23	31.46	4.58	5.54	6.62	7.67	9.38	10.47	12.20
OO/C/H[c]	−21.72	36.60	8.60	9.51	10.27	10.86	11.76	12.35	13.15

[a] THERM group database. [b] Updated group values from Sebbar et al.[81] [c] Updated group values: $\Delta_f H°$(298 K) taken from Simmie et al.,[72] $S°$(298 K) and $C_p°$(T) deduced from thermochemical properties of methylhydroperoxide taken from Dorofeeva et al.[82] and the equation below: X(OO/C/H) = X(methylhydroperoxide) − X(C/H3/OO) − X(OI) + R ln 3

**Table 8. Target Group Values Calculated Using Thermochemical Properties from the Literature**

			cal K^{-1} mol^{-1}						
target group and species[a] used	$\Delta_f H°$(298 K), kcal mol^{-1}	$S°$(298 K)	$C_p°$(300 K)	$C_p°$(400 K)	$C_p°$(500 K)	$C_p°$(600 K)	$C_p°$(800 K)	$C_p°$(1000 K)	$C_p°$(1500 K)
C/CB/H2/OO	−5.29	6.72	5.23	7.20	8.93	10.29	12.02	13.10	14.45
CB/CO	5.27	−8.05	5.80	6.90	7.62	7.96	8.30	8.52	8.18
benzylhydroperoxide[b]	−5.00	93.28	32.70	42.05	50.18	56.80	66.44	72.94	82.23
benzaldehyde[c]	−7.46	79.68	26.58	34.64	41.54	47.13	55.38	61.04	69.03

[a] Species used to determine the target group values. [b] Thermochemical properties of benzylhydroperoxide taken from da Silva et al.[62] and used to determine the C/CB/H2/OO group values. [c] Thermochemical properties of benzaldehyde taken from Sebbar et al.[81] and used to determine the CB/CO group values.

due to the existence of two optical isomers as in the case of a hydroperoxide.

The methodologies used to determine $\Delta_f H°$(298 K), $C_p°$(T), and $S°$(298 K) values for a target group as well as for the OO/C/H group are described in the two following sub-subsections.

3.5.1. Determination of $\Delta_f H°$(298 K) and $C_p°$(T) Group Values. The contributions to $\Delta_f H°$(298 K) and $C_p°$(T) for a target group are determined using $\Delta_f H°$(298 K) and $C_p°$(T) values of a molecule containing that group, as well as $\Delta_f H°$(298 K) and $C_p°$(T) values of reference groups included in the decomposition in groups (DG) of the molecule. Let us take the example of $\Delta_f H°$(298 K) and $C_p°$(T) value determination for the ORT/CH2OOH/ME target group, which takes into account the interaction between the substituents methylhydroperoxy and methyl in the ortho position on a benzenic cycle. This target group is included in the DG of 2-methylbenzylhydroperoxide (**4**), which is:

2 CB/C, 4 CB/H, 1 OO/C/H, 1 C/CB/H2/OO,

1 C/CB/H3, 1 ORT/CH2OOH/ME
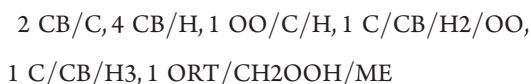
Thus, $\Delta_f H°$(298 K) and $C_p°$(T) values of ORT/CH2OOH/ME group are calculated by eq 11.

$$X(\text{ORT/CH2OOH/ME}) = X(\text{2-methybenzylhydroperoxide})$$

$$- 2X(\text{CB/C}) - 4X(\text{CB/H}) - X(\text{OO/C/H})$$

$$- X(\text{C/CB/H2/OO}) - X(\text{C/CB/H3}) \qquad (11)$$

where $X = \Delta_f H°$(298 K) or $C_p°$(T). Table 9 lists the equations used to determine $\Delta_f H°$(298 K) and $C_p°$(T) group values for all target groups.

3.5.2. Determination of $S°$(298 K) Group Values. The contribution to $S°$(298 K) for a target group is determined using the $S°$(298 K) value of a molecule containing that group and the values of reference groups included in the DG of the molecule. The $S°$(298 K) group value excludes contributions from symmetry and the existence of optical isomers. Indeed, when the GAM is applied to a species, these contributions must be added to the sum of $S°$(298 K) group values of the groups contained in the DG of the considered species. As a result, two supplementary terms appear in the equation used to determined the $S°$(298 K)

Table 9. Equations Used To Determine the Target Group Values

target group	X	equation
C/CB/H2/OO	$\Delta_f H°(298\ K)$ or $C_p°(T)$	$X(C/CB/H2/OO) = X(\text{benzylhydroperoxide}) - X(CB/C) - 5X(CB/H) - X(OO/C/H)$
	$S°(298\ K)$	$X(C/CB/H2/OO) = X(\text{benzylhydroperoxide}) - X(CB/C) - 5X(CB/H) - X(OO/C/H) + R\ln 2$
CB/CO	$\Delta_f H°(298\ K)$ or $C_p°(T)$	$X(CB/CO) = X(\text{benzaldehyde}) - 5X(CB/H) - X(CO/CB/H)$
	$S°(298\ K)$	$X(CB/CO) = X(\text{benzaldehyde}) - 5X(CB/H) - X(CO/CB/H) + R\ln 2$
ORT/CH2OOH/ME	$\Delta_f H°(298\ K)$ or $C_p°(T)$	$X(ORT/CH2OOH/ME) = X(\text{2-methylbenzylhydroperoxide}) - 2X(CB/C) - 4X(CB/H) - X(OO/C/H)$ $- X(C/CB/H2/OO) - X(C/CB/H3)$
	$S°(298\ K)$	$X(ORT/CH2OOH/ME) = X(\text{2-methylbenzylhydroperoxide}) - 2X(CB/C) - 4X(CB/H) - X(OO/C/H) - X(C/CB/H2/OO)$ $- X(C/CB/H3) - R\ln 2 + R\ln 3$
ORT/ET/ME	$\Delta_f H°(298\ K)$ or $C_p°(T)$	$X(ORT/ET/ME) = X(\text{1-ethyl-2-methybenzene}) - 4X(CB/H) - X(C/C/CB/H2) - X(C/C/H3)$ $- X(C/CB/H3) - 2X(CB/C)$
	$S°(298\ K)$	$X(ORT/ET/ME) = X(\text{1-ethyl-2-methybenzene}) - 4X(CB/H) - X(C/C/CB/H2) - X(C/C/H3)$ $- X(C/CB/H3) - 2X(CB/C) + R\ln 9$
ORT/CHO/OH	$\Delta_f H°(298\ K)$ or $C_p°(T)$	$X(ORT/CHO/OH) = X(\text{2-hydroxybenzaldehyde}) - X(CB/CO) - X(CB/O) - 4X(CB/H)$ $- X(CO/CB/H) - X(O/CB/H)$
	$S°(298\ K)$	$X(ORT/CHO/OH) = X(\text{2-hydroxybenzaldehyde}) - X(CB/CO) - X(CB/O) - 4X(CB/H)$ $- X(CO/CB/H) - X(O/CB/H)$
ORT/CHO/CH2OOH	$\Delta_f H°(298\ K)$ or $C_p°(T)$	$X(ORT/CHO/CH2OOH) = X(\text{2-(hydroperoxymethyl)benzaldehyde}) - X(CB/CO) - X(CB/C) - 4X(CB/H)$ $- X(CO/CB/H) - X(C/CB/H2/OO) - X(OO/C/H)$
	$S°(298\ K)$	$X(ORT/CHO/CH2OOH) = X(\text{2-(hydroperoxymethyl)benzaldehyde}) - X(CB/CO) - X(CB/C)$ $- 4X(CB/H) - X(CO/CB/H) - X(C/CB/H2/OO) - X(OO/C/H) - R\ln 2$
MET/CHO/OH	$\Delta_f H°(298\ K)$ or $C_p°(T)$	$X(MET/CHO/OH) = X(\text{3-hydroxybenzaldehyde}) - X(CB/CO) - X(CB/O) - 4X(CB/H)$ $- X(CO/CB/H) - X(O/CB/H)$
	$S°(298\ K)$	$X(MET/CHO/OH) = X(\text{3-hydroxybenzaldehyde}) - X(CB/CO) - X(CB/O) - 4X(CB/H)$ $- X(CO/CB/H) - X(O/CB/H)$
ME/ME/OH123	$\Delta_f H°(298\ K)$ or $C_p°(T)$	$X(ME/ME/OH123) = X(\text{2,3-dimethylphenol}) - X(CB/O) - 2X(CB/C) - 3X(CB/H)$ $- 2X(C/CB/H3) - X(O/CB/H)$
	$S°(298\ K)$	$X(ME/ME/OH123) = X(\text{2,3-dimethylphenol}) - X(CB/O) - 2X(CB/C) - 3X(CB/H)$ $- 2X(C/CB/H3) - X(O/CB/H) + R\ln 9$

value of a target group: a term $-R\ln n(\text{oi})$ and a term $+R\ln \sigma$ where $R = 1.987$ cal K^{-1} mol^{-1}, $n(\text{oi})$ is the number of optical isomers for the species, and σ is its symmetry number. The term $R\ln \sigma$ is a correction to the rotational entropy due to the existence of symmetry axes in the species. The easiest way to calculate σ is to multiply the external number of symmetry, σ_{ext}, of the species by its internal symmetry number, σ_{int}, whose value depends on the presence of symmetrical internal rotors.

Let us take again the example of $S°(298\ K)$ value determination for the ORT/CH2OOH/ME target group. As 2-methyl-benzylhydroperoxide (**4**) is an hydroperoxide, an entropy of mixing equal to $R\ln 2$ (due to the existence of two optical isomers[83]) must be added to the sum of $S°(298\ K)$ group values of this species. As species **4** has no external symmetry axis, $\sigma_{\text{ext}} = 1$. The C$_6$H$_5$—CH$_3$ bond is a 3-fold symmetry axis leading to $\sigma_{\text{int}} = 3$ and thus $\sigma = \sigma_{\text{int}}\ \sigma_{\text{ext}} = 1 \times 3 = 3$. The term $R\ln 3$ must be subtracted to the sum of $S°(298\ K)$ group values of this species. $S°(298\ K)$ of 2-methylbenzylhydroperoxide is then given by

eq 12.

$$X(\text{2-methylbenzylhydroperoxide}) = 2X(CB/C) + 4X(CB/H) + X(OO/C/H) + X(C/CB/H2/OO) + X(C/CB/H3) + X(ORT/CH2OOH/ME) + R\ln 2 - R\ln 3 \tag{12}$$

where $X = S°(298\ K)$.

Finally, $S°(298\ K)$ value of ORT/CH2OOH/ME group is calculated by eq 13

$$X(ORT/CH2OOH/ME) = X(\text{2-methylbenxylhydroperoxide}) - 2X(CB/C) - 4X(CB/H) - X(OO/C/H) - X(C/CB/H2/OO) - X(C/CB/H3) - R\ln 2 + R\ln 3 \tag{13}$$

where $X = S°(298\ K)$. Table 9 lists the equations used to determine $S°(298\ K)$ group values for all target groups.

Table 10 summarizes the group values of target interaction groups. In absolute value, $\Delta_f H°(298\ K)$ group values of interaction group are lower than 2 kcal mol^{-1} except for the ORT/CHO/OH (-8.64 kcal mol^{-1}) and MET/CHO/OH

607

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Table 10. Target Group Values Calculated Using Thermochemical Properties of Target Species Considered in this Work

target group	$\Delta_f H°$(298 K), kcal mol^{-1}	cal K^{-1} mol^{-1}							
		$S°$(298 K)	$C_p°$(300 K)	$C_p°$(400 K)	$C_p°$(500 K)	$C_p°$(600 K)	$C_p°$(800 K)	$C_p°$(1000 K)	$C_p°$(1500 K)
ORT/CH2OOH/ME	−1.08	−4.65	1.45	3.11	2.53	1.96	1.13	0.70	0.50
ORT/ET/ME	0.97	−4.23	0.74	0.71	0.81	0.85	0.78	0.71	0.82
ORT/CHO/OH	−8.64	−5.35	−1.28	−1.26	−0.90	−0.46	0.43	1.40	3.34
ORT/CHO/CH2OOH	−1.65	−7.87	0.05	6.21	5.12	4.04	2.34	2.37	0.71
MET/CHO/OH	−2.77	−2.86	0.03	1.30	1.06	0.97	0.74	0.66	0.50
ME/ME/OH123	−0.31	−2.76	1.50	1.48	1.36	1.22	0.78	0.57	0.15

groups (−2.77 kcal mol^{-1}). The high negative value for the ORT/CHO/OH group can be attributed to a stabilization by hydrogen bond between the H atom of hydroxyl function and the O atom of carbonyl function (see subsection 3.2). $\Delta_f H°$(298 K) group values are all negative except that of ORT/ET/ME group: we can note that the similar ORT/ME/ME group in THERM AG datatabase has also a positive $\Delta_f H°$(298 K) group value (0.74 kcal mol^{-1}). $S°$(298 K) group values are all negative with the lowest value (−7.87 cal K^{-1} mol^{-1}) for the ORT/CHO/CH2OOH group. $C_p°$(T) values are relatively small except those of the ORT/CHO/CH2OOH group between 400 and 1000 K and those of ORT/CH2OOH/ME group between 400 and 600 K.

4. CONCLUSION

The thermochemical properties, $\Delta_f H°$(298 K), $S°$(298 K), and $C_p°$(300 K $\leq T \leq$ 1500 K), of ten target species involved in the o-xylene low-temperature oxidation scheme have been determined using quantum chemistry methods. $\Delta_f H°$(298 K) values are weighted averages across the values calculated using five isodesmic reactions and five composite calculation methods: CBS-QB3, G3B3, G3MP2, G3, and G4. The uncertainty in $\Delta_f H°$(298 K) has been evaluated by taking into account the uncertainty in $\Delta_f H°$(298 K) of reference species involved in the isodesmic reactions and the uncertainty in standard reaction enthalpies of isodesmic reactions, which has been deduced from a statistical analysis using Student's t distribution. $S°$(298 K) and $C_p°$(T) of target species have been calculated from molecular properties optimized at the B3LYP/6-311G(d,p) level of theory and statistical thermodynamics through evaluation of translational, rotational, vibrational, and electronic partition functions. $S°$(298 K) and $C_p°$(300 K) values have been evaluated using the rigid-rotor-harmonic-oscillator model. $C_p°$(T) values at $T \geq$ 400 K have been calculated by treating separately internal rotational contributions and translational, external rotational, vibrational, and electronic contributions. The obtained thermochemical properties of six target species have been used to develop six new additivity groups, taking into account the interaction between two substituents in ortho (ORT/CH2OOH/ME, ORT/ET/ME, ORT/CHO/OH, ORT/CHO/CH2OOH), or meta (MET/CHO/OH) positions, and the interaction between three substituents (ME/ME/OH123) located one beside the other (positions numbered 1, 2, 3) for two- or three-substituted benzenic species. Two other groups have been also developed using the thermochemical properties of benzenic species taken from the literature: the C/CB/H2/OO and the CB/CO groups. These groups can be included in the THERM additivity group database to extend the capacities of the group additivity method to deal with substituted benzenic species.

■ ASSOCIATED CONTENT

ⓢ Supporting Information. Optimized geometry at B3LYP/6-311G(d,p) level of theory and optimized Cartesian coordinates at the different levels of theory (Table 1S−10S) as well as calculated unscaled vibrational frequencies at B3LYP/6-311G(d,p) level of theory (Table 11S) of the target species. This material is available free of charge via the Internet at http://pubs.acs.org.

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