Enthalpies of Formation and Group Additivity of Alkyl Peroxides and Trioxides

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Alkyl peroxides, trioxides, and the corresponding radicals are important in atmospheric chemistry, photochemical smog formation, and combustion processes, but accurate and widely accepted enthalpy data for these species are not available. In this work we verify enthalpy data for several compounds and derive the corresponding group values for use in the group additivity method. Isodesmic reactions and ab initio calculations (MP4SDTQ/6-31G*//MP2/6-31G* and G2) are used to determine enthalpies of formation for the following compounds (in kcal mol^{-1}): CH_3OOH (−31.8), C_2H_5OOH (−39.9), *i*PrOOH (*i*Pr = $(CH_3)_2$-CH−, −49.0), $(CH_3)_3COOH$ (*t*Bu = $(CH_3)_3C$−, −58.4), *i*PrOO• (−15.1), *t*BuCOO• (−25.2), CH_3OOCH_3 (−31.0), $C_2H_5OOC_2H_5$ (−47.2), *i*PrOO*i*Pr, (−65.4), *t*BuOO*t*Bu (−84.2), HOOOH (−23.0), CH_3OOOH (−22.2), CH_3OOOCH_3 (−21.4). Our results on isodesmic reactions indicate that group additivity is an accurate method to estimate enthalpies ($\Delta H_f{}^\circ{}_{298}$) of alkyl peroxides and trioxides. Bond enthalpies are determined as follows: HOOO−H (82.6), CH_3O_2−H (86.6), $C_2H_5O_2$−H (86.1), *i*PrO_2−H (86.0), *t*BuO_2−H (85.3), HOO−OH (35.8), CH_3O−OCH_3 (38.8), CH_3OO−OH (34.2), CH_3O−OOH (29.6), CH_3O−$OOCH_3$ (28.0), *i*Pr−OO (36.6), *t*Bu−OO (37.5). The recommended enthalpy group values of (O/C/O) and (O/O_2) are −5.5 and 9.6 kcal mol^{-1}, respectively.

Introduction

Alkyl peroxides and trioxides and the corresponding radicals are important for hydrocarbon oxidation in the atmosphere and in low-temperature combustion process. Thermodynamic parameters which are accurate and accepted by scientific community for these species are not available to use in evaluating reaction pathways, rate constants and equilibrium constants. There have been several experimental studies, molecular mechanics (MM) and molecular orbital (MO) calculations on alkyl peroxy radicals[1−9] and alkyl hydroperoxides.[9−19] Results of these studies are not in full agreement and do not agree with the generic estimation method, group additivity (GA), to better than 3 to 7 kcal/mol.[20]

Benson's group values for alkyl peroxides and radicals are primarily derived as follows:

I. $\Delta H_f{}^\circ{}_{298}$(HOOH) = −32.6 kcal mol^{-1} [21] is used to define the group (O/H/O) = −16.3 kcal mol^{-1}.

II. The group (O/C/O) = −4.5 kcal mol^{-1} is an average value derived from the enthalpy data for alkyl peroxides and hydroperoxides available to Benson and Shaw[11] in 1970.

III. Other groups needed for peroxides are either assigned, e.g. (C/H_3/O) = −10.1 kcal mol^{-1} the same as (C/H_3/C) group; or obtained from the data of alcohols, e.g. (C/C/H_2/O).

The enthalpy of formation for CH_3OOH, as an example, is determined as −30.9 kcal mol^{-1} using the above group values (O/C/O), (O/H/O), and (C/H_3/O).

$\Delta H_f{}^\circ{}_{298}$(HOO•) is also determined to be 3.5 kcal mol^{-1} by Shum and Benson [1] based on the experimental data available before 1983. DH°$_{298}$(HOO−H) = 88.2 kcal mol^{-1} is then obtained and assumed equal to the generic DH°$_{298}$(ROO−H) bond energy of alkyl hydroperoxides. Since there are more experimental data on enthalpies of alkyl peroxy radicals relative to alkyl hydroperoxides, $\Delta H_f{}^\circ{}_{298}$(ROO•) is often used with DH°$_{298}$(HOO−H) = 88.2 kcal mol^{-1} to estimate $\Delta H_f{}^\circ{}_{298}$(ROOH). For example, Kondo and Benson[13] performed a measurement for $\Delta H_f{}^\circ{}_{298}$($CH_3OO$) = 5.5 ± 1.0 kcal mol^{-1}, and $\Delta H_f{}^\circ{}_{298}$($CH_3OOH$) = −30.6 kcal mol^{-1} is then obtained using DH°$_{298}$(CH_3O_2−H) = 88.2 kcal mol^{-1} and $\Delta H_f{}^\circ{}_{298}$(H) =52.1 kcal mol^{-1}. This supports their estimation of $\Delta H_f{}^\circ{}_{298}$($CH_3OOH$) = −30.9 kcal mol^{-1} determined using the GA method.

The enthalpy of formation for CH_3OO is later remeasured as 2.41 ± 0.80 kcal mol^{-1},[4] which is recently revised by Knyazev and Slagle to be 2.15 ± 1.22 kcal mol^{-1}.[22] Their values are about 3 kcal mol^{-1} lower (more stable) than Benson's value.[13] A recent ab initio study[23] by Jungkamp and Seinfeld also reports $\Delta H_f{}^\circ{}_{298}$($CH_3OO$) = 2.24 kcal mol^{-1} as calculated at the G2-(RCC) level of theory, which is in very good agreement with the data reported by Knyazev and Slagle. If the bond enthalpy DH°$_{298}$(CH_3O_2−H) = 88.2 kcal mol^{-1} is used with $\Delta H_f{}^\circ{}_{298}$($CH_3OO$) = 2.2 kcal mol^{-1}, a lower enthalpy value, $\Delta H_f{}^\circ{}_{298}$($CH_3OOH$) = −33.9 kcal mol^{-1}, is obtained. This enthalpy value will result in a value of −7.5 kcal mol^{-1} for the (O/C/O) group while the group values of (C/H_3/O) and (O/H/O) are unchanged. These variations suggest that a clear determination and validation of the corresponding group values of peroxide species is needed.

Benassi et al.[24] proposed a revised set of group contributions: (O/C/O) = −6.52 kcal mol^{-1}, (O/C_p/O) = −5.17 kcal mol^{-1}, (O/C_s/O) = −4.24 kcal mol^{-1}, (O/C_t/O) = −4.11 kcal mol^{-1}, to fit $\Delta H_f{}^\circ{}_{298}$ data in the literature for CH_3OOH, C_2H_5OOH, *i*C_3H_7OOH and *t*C_4H_9OOH, respectively. This suggests that Benson's group additivity scheme may not be sufficient to predict the enthalpies of formation on all types of alkyl peroxides since different (O/C_X/O) groups (X = p, s, t, ... etc.) are needed. The enthalpy data used by Bennassi et al. are either from literature or the authors' calculation using the molecular mechanics methods (MM3).[24]

Enthalpies are needed for determination of reaction and process energies, for development of elementary reaction mechanisms, for evaluation of reaction pathways, and for calculation of chemical equilibrium constants. Group additivity is an important method for the estimation of thermodynamic properties of complex, high molecular weight species such as

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TABLE 1: Enthalpy Data Used in Isodesmic Reactions to Determine $\Delta H_f°_{298}$ of Other Species

compound	$\Delta H_f°_{298}$ in kcal mol^{-1}	source
HOO•[a]	3.5	ref 20
HOOH[a]	−32.6	ref 21
CH_3OO•	2.2	ref 22
CH_3OH	−48.08	ref 10

[a] $DH°_{298}(HO_2{-}H) = 88.2$ kcal mol^{-1} is determined using these data and $\Delta H_f°_{298}(H) = 52.1$ kcal mol^{-1}.

TABLE 2: Group Values

group	$\Delta H_f°_{298}$ in kcal mol^{-1}	source
Group values adopted from literature used in the group validation:		
O/H/O	−16.3	*a*
C/C/H_3	−10.0	ref 31
C/H_3/O	−10.0	ref 31
C/C/H_2/O	−8.1	ref 31
C/C_2/H/O	−7.2	ref 31
C/C_3/O	−6.6	ref 31
Group values derived in this work:		
O/C/O	−5.5	
O/O_2	9.6	

[a] Derived from 0.5 $\Delta H_f°_{298}$(HOOH); see Table 1.

alkyl and dialkyl peroxy compounds, and aromatic peroxy compounds such as: benzene-OH−O2 adduct (hydroxyl-2,4-hexadiene-6-peroxy radical) and toluene-OH−O2 adduct (hydroxyl-2-methyl-2,4-hexadiene-6-peroxy radical), which are primary reaction intermediates of atmospheric photooxidation of aromatics.[25,26] Ab initio calculations are not appropriate for these species, because of the need for extensive computing resource and time.

The group (O/O_2) is needed for the reaction products of ozone with olefins, and the effort addressed on (O/O_2) group is less than (O/C/O) and (O/H/O) groups. In this work we calculate enthalpies of formation for several compounds which are important to derive the corresponding group values and verify the application of group additivity to dialkyl peroxides and trioxides, and alkyl hydroperoxides.

Calculations and Results

All ab initio MO calculations are performed using Gaussian 94 system of programs.[27] Molecular geometry is fully optimized at the HF/6-31G* and MP2(fc)/6-31G* or MP2(full)/6-31G* levels of theory using the default algorithm and redundant internal coordinates.[28] MP2(fc) denotes “frozen-core” MP2 calculation that inner-shell electrons are excluded from correlation calculations, and MP2(full) indicates all electrons are included in correlation calculations.[28] The unrestricted Hartree−Fock method is used for all open-shell free radicals. The default optimization criteria are employed. Harmonic vibrational frequencies are calculated at the HF/6-31G* level of theory and zero-point vibrational energies (ZPE) are scaled by 0.89 in the calculation of reaction enthalpies. Single-point energy calculations are carried out at the MP4STDQ/6-31G*//MP2(fc)/6-31G*, or mp4SDTQ/6-311 G**//MP2(full)/6-31G*, or QCISD(T)/6-311G**//MP2(full)/6-31G* level of theory,[28] depending on the size of the molecules. MP4STDQ method is simply denoted as MP4 hereafter.

The method of isodesmic reaction relies upon the similarity in bonding environment of the reactants and products that leads to cancellation of systematic errors in the ab initio MO calculation.[29] An isodesmic reaction will lead to more accurate results if in addition to the conservation of chemical bonds the correlations of next-nearest-neighbor atoms in reactants and products are also conserved. We implement this by selecting isodesmic reactions where the number of each of the groups is equal in reactants and products. A group is defined as a polyvalent atom (ligancy ≥ 2) in a molecule together with all of its ligands.[30] A reaction which matches these criteria is termed an isodesmic reaction with “group balance”. We expect that ab initio calculations on reaction enthalpies of group balanced isodesmic reactions, performed at the theory levels higher than MP4/6-31G*//MP2/6-31G* will lead to minor differences for the reaction energies from the values reported in the present study.

Enthalpies of formation of the primary species adopted from literature which are used to determine $\Delta H_f°_{298}$ values of species studied in this work are listed in Table 1. Group values are then validated using the calculated $\Delta H_f°_{298}$ data and primary alkane groups adopted from the work by Cohen and Benson.[31] All group values are listed in Table 2.

Total electronic energies, G2 entalpies, zero point vibrational energies (ZPE), and thermal correction for each compound are listed in Table 3. Calculations of ZPE and thermal corrections do not incorporate a substitution of contributions from the hindered internal rotor (HIR) in place of the calculated torsion frequency. ZPEs of molecules considered in the present study are in the range from 20 to 90 kcal mol^{-1} and the contribution of an HIR to ZPE is usually less than 0.6 kcal mol^{-1} which corresponds to a harmonic torsional frequency of 400 cm^{-1}. We assume deviations in the ZPE by using harmonic torsion frequency instead of HIR model are not important when isodesmic reactions with group balance are used to derive enthalpy values, since deviations on both reactants and products will compensate. Thermal corrections of corresponding torsional frequencies 143.7, 201.6, and 223.0 cm^{-1} of CH_3CH_2OOH, for example, are 0.41, 0.35, and 0.33 kcal mol^{-1}, respectively. Thermal corrections determined using HIR model and rotational barriers obtained at the MP2/6-31G*//MP2/6-31G* level of theory[14] are 0.51, 0.30, and 0.37, respectively. The total difference between these two methods on thermal correction is 0.09 kcal mol^{-1}. Again this deviation is reduced when isodesmic reactions are used to derive enthalpy data.

Theoretical reaction enthalpies which include thermal corrections are determined at different theory levels and are illustrated in Table 4. The comparison of enthalpies of formation determined in this work to the data in the literature is listed in Table 5. Recommended bond enthalpies are listed in Table 6.

I. $D°_{298}(CH_3OO{-}H)$, $\Delta H_f°_{298}(CH_3OOH)$, $\Delta H_f°_{298}(CH_3OOCH_3)$, and (O/C/O). $\Delta H_f°_{298}(CH_3OOH)$ is derived from $\Delta H_f°_{298}(CH_3OO)$, and $DH°_{298}(CH_3O_2{-}H)$. We first determine the difference of $DH°_{298}(CH_3O_2{-}H)$ and $DH°_{298}(HO_2{-}H)$ using reaction 1. Reaction enthalpy determined using the G2 method indicates that the bond enthalpy $DH°_{298}(CH_3O_2{-}H)$ is about 1.6 kcal/mol lower than $DH°_{298}(HO_2{-}H)$. Bond lengths determined using the MP2(full)/6-31G* method also show the same trend. The bond length $CH_3O_2{-}H = 0.9767$ Å is about 0.002 longer (therefore weaker) than $HO_2{-}H$ (0.9755 Å). $DH°_{298}(CH_3O_2{-}H)$ is determined to be $88.2-1.6 = 86.6$ kcal mol^{-1}, using $DH°_{298}(HO_2{-}H) = 88.2$ kcal mol^{-1}.[20]

$$CH_3OO + H_2O_2 \rightarrow CH_3OOH + HO_2 \qquad (1)$$

$\Delta H_f°_{298}(CH_3OOH)$ is subsequently determined as −32.3 kcal mol^{-1} using $DH°_{298}(CH_3O_2{-}H) = 86.6$ and $\Delta H_f°_{298}(CH_3OO) = 2.2$ kcal mol^{-1}. This value is in reasonable agreement with the value reported by Jungkamp and Seinfeld: $\Delta H_f°_{298}(CH_3OOH) = -31.71$ kcal mol^{-1},[23] which is determined via atomization energy calculated at the G2 level of theory.

TABLE 3: Total Energies (in Hartree) at Different Levels of Theory, G2 Enthalpies (in Hartree), and Zero-Point Energies (in kcal mol^{-1}) and Thermal Corrections (in kcal mol^{-1})

	total energies[a]								
	hf	mp2(fc)	mp4/mp2(fc)	mp2(full)	mp4/mp2(ful1)	qcisd(t)	G2[b]	zpe[c]	therm. corr[d]
alcohols									
CH_3OH	−115.0354190	−115.3461353	−115.3738673				−115.530600	34.72	2.64
$(CH_3)_2CHOH$	−193.1154160	−193.6896390	−193.7488344					72.78	3.85
$(CH_3)_3COH$	−232.1534710	−232.8627906	−232.9374460					91.34	4.56
peroxy radicals									
HOO•	−150.1705300			−150.5023651	−150.621172	−150.6152009	−150.724113	9.85	2.38
CH_3OO•	−189.2023120	−189.6584785	−189.7003812	−189.6680179	−189.8256395	−189.8196030	−189.943032	29.29	2.91
CH_3CH_2OO•	−228.2427062	−228.8304226	−228.8881533	−228.8448061	−229.0344383	−229.0382035		48.43	3.52
$(CH_3)_2CHOO$•	−267.2818714	−268.0028727	−268.0762370					67.25	4.27
$(CH_3)_3COO$•	−306.3197618	−307.1769083	−307.265721					85.83	4.99
peroxides									
HOOH	−150.7647868	−151.1301265	−151.1507487	−151.1349184	−151.2671644	−151.2546995	−151.361602	18.39	2.58
CH_3OOH	−189.7967190	−190.2900714	−190.3277685	−190.2997361	−190.4694992	−190.4570650	−190.577106	37.55	3.2
CH_3OOCH_3	−228.8287659	−229.4509321	−229.5053608	−229.4655202	−229.6720150	−229.6593630		56.69	3.96
CH_3CH_2OOH	−228.8367278	−229.4609188	−229.5146298	−229.4756237	−229.6753239	−229.6749884		56.66	3.91
$CH_3CH_2OOC_2H_3$	−306.9073093	−307.7933119	−307.8797664					94.89	5.32
$(CH_3)_2CHOOH$	−267.8756609	−268.6336575	−268.7026436					75.46	4.59
$(CH_3)_3COOH$	−306.9124035	−307.8065451	−307.8910094					94.08	5.29
HOOOH	−225.5336258	−226.0834859	−226.1141341				−226.419688	21.46	2.87
CH_3OOOH	−264.5653490	−265.2443288	−265.2921581				−265.636278	40.54	3.59
CH_3OOOCH_3	−303.5968209	−304.4054043	−304.4704568					59.53	3.20

[a] Total energies in Hartree. Theory levels: hf = HF/6-31G*//HF/6-31G*, mp2(fc) = MP2(frozen-core)/6-31G*//MP2(frozen-core)/6-31G*, mp2(full) = MP2(full)/6-31G*//MP2(full)/6-31G*, mp4/mp2(full) = MP4SDTQ/6-311G**//MP2(full)/6-31G*, qcisd(t) = QCISD(T)/6-311G**//MP2(full)/6-31G*. [b] G2 enthalpies in Hartree, which include full thermal correction and zero-point energy at $T = 298.15$ K. [c] zpe: Unscaled zero-point vibrational energies in kcal mol^{-1}. In the calculation of reaction enthalpies, zpe is scaled by 0.89. [d] Therm. corr.: Thermal corrections are calculated as follows for $T = 298.15$ K: $H°_T - H°_0 = H_{trans}(T) + H_{rot}(T) + \Delta H_{vib}(T) + RT$; $H_{trans}(T) = (3/2)\ RT = 0.8886$ kcal/mol, $H_{rot}(T) = (3/2)\ RT = 0.8886$ kcal/mol, $\Delta H_{vib}(T) = N_A h \Sigma \upsilon_i/(e^{h\upsilon_i/kT} - 1)$, where N_A is the Avogadro constant, h is the Planck constant, k is the Boltzmann constant, and υ_i is vibrational frequencies. $RT = 0.5924$ kcal/mol.

TABLE 4: Reaction Enthalpies (in kcal mol^{-1}) at 298.15 K[a]

		theory levels[b]						
	reaction	hf	mp2(fc)	mp4/mp2(fc)	mp2(full)	mp4/mp2(full)	qcisd(t)	G2
1	$CH_3OO + HOOH \rightarrow CH_3OOH + HO_2$	−0.25			0.37	1.18	1.12	1.55
2	$CH_3OOCH_3 + HOOH \rightarrow 2CH_3OOH$	−0.06			0.48	−0.01	−0.17	
3	$C_2H_5OO + CH_3OOH \rightarrow C_2H_5OOH + CH_3OO$	0.34	0.79	0.67			0.52	
4	$C_2H_5OOH + CH_3OOH \rightarrow C_2H_5OH + CH_3OOH$	0.23	−0.10	−0.15				
5	$(CH_3)_2CHOOH + CH_3OH \rightarrow (CH_3)_2CHOH + CH_3OOH$	−0.71	0.00	−0.11				
6	$(CH_3)_3COOH + CH_3OH \rightarrow (CH_3)_3COH + CH_3OOH$	−1.58	−0.20	−0.30				
7	$(CH_3)_2CHOO + CH_3OOH \rightarrow (CH_3)_2CHOOH + CH_3OO$	0.38	0.50	0.61				
8	$(CH_3)_3COO + CH_3OOH \rightarrow (CH_3)_3COOH + CH_3OO$	1.10	1.22	1.31				
9	$C_2H_5OOC_2H_5 + HOOH \rightarrow 2C_2H_5OOH$	−0.89	0.71	0.75				
10	$C_2H_5OOC_2H_5 + 2CH_3OOH \rightarrow CH_3OOCH_3 + 2C_2H_5OOH$	−0.93	0.42	0.42				
11	$2HOOH \rightarrow HOOOH + HOH$							−15.53
12	$2CH_3OOH \rightarrow CH_3OOOH + CH_3OH$							−7.95
13	$CH_3OOH + HOOOH \rightarrow CH_3OOOH + HOOH$							−0.68
14	$HOOO + HOOH \rightarrow HOOOH + HOO$							5.61
15	$CH_3OOCH_3 + CH_3OOOH \rightarrow CH_3OOOCH_3 + CH_3OOH$	0.24	−0.25	−0.56				
16	$CH_3OOCH_3 + HOOOH \rightarrow 2CH_3OOOH$	−0.14	0.10	0.13				

[a] Reaction enthalpies include thermal correction and zero-point energy correction. [b] See Table 3 footnote *a* for the explanation of theory levels.

TABLE 5: Comparison of Enthalpies of Formation (in kcal mol^{-1})

	this work	ref 11	ref 12	ref 17	ref 18	ref 19	ref 23	ref 24	ref 31[a]	ref 34	Nangia et al.[b]
HOOOH	−23.0						−23.49		−13.6		−15.7
CH_3OOH	−31.8	−31.3		−30.5			−31.71	−33.4	−30.8		−31.3
CH_3OOOH	−22.2						−22.40		−11.7		−14.5
CH_3OOCH_3	−31.0			−31.0				−33.2	−29.0	−30.1	−30.0
C_2H_5OOH	−39.9						−39.71		−38.9		
$C_2H_5OOC_2H_5$	−47.2			−47.3				−47.5	−45.2	−46.1	
iC_3H_7OOH	−49.0			−49.0	−49.3			−47.5	−43.9		
tC_4H_9OOH	−58.4		−58.8	−57.1				−57.6	−57.4		
$iC_3H_7OOiC_3H_7$	−65.4			−65.4	−66.1			−62.8	−65.2		
$tC_4H_9OOtC_4H_9$	−84.2					−83.4			−82.2	−81.5	

[a] Enthalpies of formation are calculated using group additivity and group values reported by Cohen and Benson in ref 31. [b] Nangia, P. S.; Benson, S. W. *J. Phys. Chem.* **1979**, *83*, 1138.

Reaction 2 is used to verify accuracy of GA in the prediction of $\Delta H_f°_{298}(CH_3OOH)$. The $\Delta H_{RXN}°_{298}(2)$ obtained at the QCISD(T) level of theory is about zero. This means the group balanced reaction 2 has generic GA properties, and the group (O/C/O) derived from $\Delta H_f°_{298}(HOOH)$ and $\Delta H_f°_{298}(CH_3OOH)$ is able to precisely determine $\Delta H_f°_{298}(CH_3OOCH_3)$ (see Table

TABLE 6: Recommended Bond Enthalpies ($DH°_{298}$) of A−B in Kcal Mol^{-1}

A	B	$DH°_{298}$	A	B	$DH°_{298}$
HOOO	H	82.6	CH_3O_2	H	86.6
$C_2H_5O_2$	H	86.1	*i*PrO$_2$	H	86.0
*t*BuO$_2$	H	85.3	HOO	OH	35.8
CH_3O	OCH_3	38.8	CH_3OO	OH	34.2
CH_3O	OOH	29.6	CH_3O	$OOCH_3$	28.0
*i*Pr	OO	36.6	*t*Bu	OO	37.5

2 for group values).

$$CH_3OOCH_3 + HOOH \rightarrow 2\ CH_3OOH \qquad (2)$$

If the value $\Delta H_f°_{298}(CH_3OOH) = -32.3$ kcal mol^{-1} is selected, the (O/C/O) group is determined to be −6.0 kcal mol^{-1}, compared to Benson's value: −4.5. $\Delta H_f°_{298}(CH_3OOCH_3) = -31.8$ kcal mol^{-1} is then obtained using the GA method and (O/C/O) = −6.0 kcal mol^{-1}. This enthalpy value for dimethyl peroxide is identical with the data reported by Bach et al.,[32] which is derived from $DH°_{298}(CH_3O{-}OCH_3) = 39.43$ kcal mol^{-1} determined using the G2 method and $\Delta H_f°_{298}(CH_3O) = 3.90$ kcal mol^{-1}.[33] It is, however, 1.7 kcal/mol lower than the experimental data reported by Baker et al.: $\Delta H_f°_{298}(CH_3OOCH_3) = -30.1 \pm 0.3$ kcal mol^{-1},[34] which leads to (O/C/O) group equal to −5.0 kcal mol^{-1}. We choose the average value: −5.5 kcal mol^{-1} for (O/C/O) group.

II. $D°_{298}(CH_3CH_2OO{-}H)$ and $\Delta H_f°_{298}(CH_3CH_2OOH)$. Reaction 3 is used to compare $DH°_{298}(CH_3CH_2OO{-}H)$ and $DH°_{298}(CH_3OO{-}H)$. The $\Delta H_{RXN}°_{298}(3)$ determined using the QCISD(T)/6-311G**//MP2(full)/6-31G* method is 0.5 kcal mol^{-1} (see Table 4), i.e., $DH°_{298}(CH_3CH_2OO{-}H) = 86.1$ kcal mol^{-1}. Using the experimental data on $\Delta H_f°_{298}(CH_3CH_2OO)$: −5.2 kcal mol^{-1}, determined by Wagner et al.,[35] $\Delta H_f°_{298}(CH_3CH_2OOH) = -39.2$ kcal mol^{-1} is obtained.

$$CH_3CH_2OO + CH_3OOH \rightarrow CH_3CH_2OOH + CH_3OO \qquad (3)$$

A near zero reaction enthalpy of reaction 4 is determined at the MP4/6-31G**//MP2(fc)/6-31G* level of theory; see Table 4. This validates that GA holds for CH_3CH_2OOH, since the reaction is group balanced. The group $(C/C/H_2/O) = -8.1$ kcal mol^{-1} derived from ethanol, in use with other groups derived above, results in $\Delta H_f°_{298}(CH_3CH_2OOH) = -39.9$ kcal mol^{-1}. This value is in reasonable agreement with the above data.

$$CH_3CH_2OH + CH_3OH \rightarrow CH_3CH_2OOH + CH_3OOH \qquad (4)$$

III. $\Delta H_f°_{298}((CH_3)_2CHOOH)$ and $\Delta H_f°_{298}((CH_3)_3CHOOH)$. Benassi et al.[24] report a revised set of group contributions: (O/C/O) = −6.52 kcal mol^{-1} for CH_3OOH and CH_3OOCH_3, $(O/C_p/O) = -5.17$ kcal mol^{-1} for C_2H_5OOH and $C_2H_5OOC_2H_5$, $(O/C_s/O) = -4.24$ kcal mol^{-1} for *i*C_3H_7OOH and *i*C_3H_7OO*i*C_3H_7, $(O/C_t/O) = -4.11$ kcal mol^{-1} for *t*C_4H_9OOH and *t*C_4H_9OO*t*C_4H_9, to fit their $\Delta H_f°_{298}$ data determined using the molecular mechanics method. It suggests that generic GA is not appropriate in the prediction of $\Delta H_f°_{298}$ for primary, secondary and tertiary alkyl peroxides. We perform calculations on reactions 5 and 6 to examine if different types of (O/C/O) groups are required.

$$(CH_3)_2CHOOH + CH_3OH \rightarrow (CH_3)_2CHOH + CH_3OOH \qquad (5)$$

$$(CH_3)_3COOH + CH_3OH \rightarrow (CH_3)_3COH + CH_3OOH \qquad (6)$$

$\Delta H_{RXN}°_{298}(5) \approx 0$ and $\Delta H_{RXN}°_{298}(6) \approx 0$ are obtained (see Table 4) using the MP4/6-31G*//MP2(fc)/6-31G* method. This indicates that the (O/C/O) group derived from CH_3OOH can be used with groups derived from alcohols to precisely predict enthalpies of isopropyl and *tert*-butyl hydroperoxides, i.e., all (O/C/O) groups should be identical. $\Delta H_f°_{298}((CH_3)_2CHOOH)$ and $\Delta H_f°_{298}((CH_3)_3COOH)$ are determined using the GA method to be −49.0 and −58.4 kcal mol^{-1}, respectively. The calculated $\Delta H_f°_{298}((CH_3)_3COOH)$ value is in excellent agreement with the experimental data: −58.8 kcal mol^{-1}.[12]

Bond enthalpies: $DH°_{298}((CH_3)_2CHOO{-}H) = 86.0$ and $DH°_{298}((CH_3)_3COO{-}H) = 85.3$ are obtained according to $\Delta H_{RXN}°_{298}(7) = 0.6$ and $\Delta H_{RXN}°_{298}(8) = 1.3$ kcal mol^{-1}, determined at the MP4/6-31G*//MP2(fc)/6-31G* level of theory, respectively. $\Delta H_f°_{298}((CH_3)_2CHOO)$ and $\Delta H_f°_{298}((CH_3)_3COO)$ are subsequently determined to be −15.1 and −25.2 kcal mol^{-1}, respectively. These values lead to $DH°_{298}((CH_3)_2CH{-}OO) = 36.6$ and $DH°_{298}((CH_3)_3C{-}OO) = 37.5$ kcal mol^{-1}, using $\Delta H_f°_{298}((CH_3)_2HC) = 21.5$ kcal mol^{-1} [36] and $\Delta H_f°_{298}((CH_3)_3C) = 12.3$ kcal mol^{-1}.[36] The bond enthalpy $DH°_{298}((CH_3)_2CH{-}OO)$ is experimentally determined to be 39.7 kcal/mol by Slagle et al.,[2] and later revised by Knyazev and Slagle ro be 37.1 kcal mol^{-1}.[22] Their revised data is in good agreement with our result. Our determination on $DH°_{298}((CH_3)_3C{-}OO)$ is in reasonable agreement with the value reported by the same laboratory: 36.7 ± 1.9 kcal mol^{-1},[5] which is later revised to be 36.5 kcal mol^{-1}. Benson's estimation[20] on $DH°_{298}((CH_3)_2CH{-}OO) = 32.2 \pm 1.1$ and $DH°_{298}((CH_3)_3C{-}OO) = 31.4 \pm 1.1$ kcal mol^{-1} appears to be ca. 4 kcal mol^{-1} too low.

$$(CH_3)_2CHOO + CH_3OOH \rightarrow (CH_3)_2CHOOH + CH_3OO \qquad (7)$$

$$(CH_3)_3COO + CH_3OOH \rightarrow (CH_3)_3COOH + CH_3OO \qquad (8)$$

We believe the following data for R−OO• bond enthalpies (in kcal mol^{-1}) are reasonable and consistent: $DH°_{298}(CH_3{-}OO) = 32.7$,[4] $DH°_{298}(CH_3CH_2{-}OO) = 34.6$, $DH°_{298}((CH_3)_2CH{-}OO) = 36.6$ and $DH°_{298}((CH_3)_3C{-}OO) = 37.5$.

VI. $\Delta H_f°_{298}(C_2H_5OOC_2H_5)$, $\Delta H_f°_{298}(iC_3H_7OOiC_3H_7)$, and $\Delta H_f°_{298}(tC_4H_9OOtC_4H_9)$. Reaction 9 and 10 are used to examine if GA holds for diethyl peroxide. Results in Table 4 indicate that enthalpy of formation for diethyl peroxide can be correctly calculated using the GA method. $\Delta H_f°_{298}(C_2H_5OOC_2H_5)$ is calculated to be −47.2 kcal mol^{-1}. This value is in good agreement with data reported by Baker et al.: −46.1 ± 1.2 kcal mol^{-1}.[34]

$$C_2H_5OOC_2H_5 + HOOH = 2\ C_2H_5OOH \qquad (9)$$

$$C_2H_5OOC_2H_5 + 2\ CH_3OOH = CH_3OOCH_3 + 2\ C_2H_5OOH \qquad (10)$$

No calculations of isodesmic reactions for di-isopropyl peroxide and di-*tert*-butyl peroxide are performed. They are evaluated using GA: $\Delta H_f°_{298}(iC_3H_7OOiC_3H_7) = -64.9$ kcal mol^{-1}, and $\Delta H_f°_{298}(tC_4H_9OOtC_4H_9) = -84.2$ kcal mol^{-1}. Our data on di-*tert*-butyl peroxide is in good agreement with the literature data: −83.4 ± 0.8,[34] −84.6,[37] −83.4 kcal mol^{-1}.[38]

V. $\Delta H_f°_{298}(HOOOH)$, $\Delta H_f°_{298}(CH_3OOOH)$, (O/O_2), and $DH°_{298}(HO_3{-}H)$. Reaction 11 is used to calculate $\Delta H_f°_{298}(HOOOH)$ and its reaction enthalpy is determined to be −15.51 kcal mol^{-1} using the G2 method. $\Delta H_f°_{298}(HOOOH) = -22.94$ kcal mol^{-1} and group value $(O/O_2) = 9.7$ kcal mol^{-1} are subsequently obtained.

$$2\ HOOH \rightarrow HOOOH + HOH \qquad (11)$$

Another way to derive the (O/O_2) group value is via reaction 12, where $\Delta H_f°_{298}(CH_3OOOH)$ is determined. Reaction enthalpy of reaction 12 is determined as −7.95 kcal mol^{-1} using the G2 method and $\Delta H_f°_{298}(CH_3OOOH) = -22.35$ kcal mol^{-1} is obtained. This leads to (O/O_2) = 9.5 kcal mol^{-1}, about 0.2 kcal mol^{-1} different from the value determined using $\Delta H_f°_{298}$(HOOOH) and reaction 10. We again choose the average value for the (O/O_2) group: 9.6 kcal mol^{-1}. $\Delta H_f°_{298}$(HOOOH) and $\Delta H_f°_{298}(CH_3OOOH)$ are −23.0 and −22.2 kcal mol^{-1}, respectively, using the GA method. These values are consistent with the data determined from atomization energies at the G2M(RCC, MP2) level of theory reported by Jungkamp and Seinfeld:[23] −23.49, and −22.40 kcal mol^{-1}, respectively.

$$2\,CH_3OOH \rightarrow CH_3OOOH + CH_3OH \qquad (12)$$

Reaction 13 is used to verify whether the GA holds for both HOOOH and CH_3OOOH. $\Delta H_{RXN}°_{298}(13)$ is −0.68 kcal mol^{-1} obtained at the G2 level.

$$CH_3OOH + HOOOH \rightarrow CH_3OOOH + HOOH \qquad (13)$$

The bond enthalpies of O−H bonds in H_2O_2 and H_2O_3 are compared using the reaction 14. The results obtained using the G2 method indicate that O−H of H_2O_3 is 5.6 kcal mol^{-1} weaker than that of H_2O_2. Bond enthalpy HOOO−H is then determined to be 82.6 kcal mol^{-1}.

$$HOOO + HOOH \rightarrow HOOOH + HOO \qquad (14)$$

VI. $\Delta H_f°_{298}(CH_3OOOCH_3)$. Reactions 15 and 16 are utilized to verify the accuracy of GA in the prediction of $\Delta H_f°_{298}(CH_3OOOCH_3)$. Reaction enthalpies of reactions 15 and 16 are both nearly zero obtained at the MP4/6-31G*//MP2(fc)/6-31G* level of theory. $\Delta H_f°_{298}(CH_3OOOCH_3)$ is determined to be −21.4 kcal mol^{-1} using the GA method.

$$CH_3OOCH_3 + CH_3OOOH \rightarrow CH_3OOOCH_3 + CH_3OOH \qquad (15)$$

$$CH_3OOOCH_3 + HOOOH \rightarrow 2\,CH_3OOOH \qquad (16)$$

Discussion

The accuracy of group additivity in the prediction of $\Delta H_f°_{298}$ values for a given series of compounds relies on (1) whether compounds in the series have generic group additivity property; i.e., whether group values derived from other series of compounds can be used and (2) accurate group values.

In this work we use ab initio molecular orbital calculations to verify the GA properties for alkyl peroxides and trioxides. Results indicate that GA is an accurate approach in the prediction of enthalpy data for this class of compounds. The corresponding group values are also revised.

The use of GA is straightforward and easy. It does not require the computing resource as ab initio calculations do. Another advantage of using GA is the convenience of predicting thermodynamic properties for large molecules without loss of accuracy. The GA method serves as valuable tool for many scientists and engineers whose work involves thermodynamic characterization of elementary and overall reaction processes.

Ab initio methods provide sophisticated calculations on the electronic energies of compounds. Composite procedures based on ab initio calculations, such as G1,[39,40] G2,[41,42] G2M,[43] and the series of complete basis set methods (CBS)[44,45] can be applied to general molecular systems for determination of enthalpies of formation via atomization energies with good accuracy. These methods report an average deviation of ≤3 kcal mol^{-1}.[39−45] In an assessment of G2 and density functional theories on a set of 148 molecules, Curtiss et al.[46] reported that G2 theory is the most reliable method in the prediction of $\Delta H_f°_{298}$ data: 1.58 kcal mol^{-1} average absolute deviation and 8.2 kcal mol^{-1} maximum deviation. However, the accumulation of errors in the application of G2 theory become significant (≥3.5 kcal mol^{-1}) for larger molecules.[46−48] Glukhovtsev and Laiter [47] show more accurate enthalpies of formation can be derived using isodesmic or homodesmic reactions rather than atomization energies as in standard G2 theory. Raghavachari et al.[49] also indicate that the G2 method combined with isodesmic reaction energies can yield enthalpy values for large molecules with an accuracy of ±0.5 kcal mol^{-1}.[49]

In this work we use G2 enthalpies with isodesmic reactions to determine enthalpies of formation for CH_3OOH, HOOOH, and CH_3OOOH. The results are considered to be more accurate than using G2 theory with atomization energies. We also use isodesmic reactions with total electronic energies calculated at MP4SDTQ/6-31G*//MP2(fc)/6-31G* level of theory to verify the accuracy of group additivity in the calculation of enthalpy values for alkyl peroxides and trioxides. The GA scheme, after it is confirmed by ab initio calculations, should estimate enthalpy data with the same quality as ab initio calculations.

Summary

The general GA scheme is shown to be accurate in the prediction of enthalpy data for alkyl peroxides and trioxides by ab initio molecular orbital calculations and isodesmic reactions. The recommended enthalpy group values of (O/C/O) and (O/O_2) are −5.25 and 9.45 kcal mol^{-1}, respectively. Enthalpies of formation (in kcal mol^{-1}) for the following compounds are determined using the GA method: CH_3OOH (−31.8), C_2H_5-OOH (−39.9), *i*PrOOH (*i*Pr = $(CH_3)_2CH-$, −49.0), $(CH_3)_3$-COOH (*t*Bu = $(CH_3)_3C-$, −58.4), *i*PrOO• (−15.1), *t*BuCOO• (−25.2), CH_3OOCH_3 (−31.0), $C_2H_5OOC_2H_5$ (−47.2), *i*PrOO-*i*Pr, (−65.4), *t*BuOO*t*Bu (−84.2), HOOOH (−23.0), CH_3OOOH (−22.2), CH_3OOOCH_3 (−21.4). Recommended bond enthalpies are listed in Table 6.

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