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Enthalpies of Formation and Bond Dissociation Energies of Lower Alkyl Hydroperoxides and Related Hydroperoxy and Alkoxy Radicals

John M. Simmie,*,[†] Gráinne Black,[†] Henry J. Curran,[†] and John P. Hinde[‡]

Combustion Chemistry Centre, National University of Ireland, Galway, Ireland

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The enthalpies of formation and bond dissociation energies, D(ROO−H), D(RO−OH), D(RO−$\dot{O}$), D(R−$\dot{O}_2$) and D(R−OOH) of alkyl hydroperoxides, ROOH, alkyl peroxy, RO, and alkoxide radicals, R$\dot{O}$, have been computed at CBS-QB3 and APNO levels of theory via isodesmic and atomization procedures for R = methyl, ethyl, *n*-propyl and isopropyl and *n*-butyl, *tert*-butyl, isobutyl and *sec*-butyl. We show that D(ROO−H) ≈ 357, D(RO−OH) ≈ 190 and D(RO−$\dot{O}$) ≈ 263 kJ mol^{-1} for all R, whereas both D(R−$\dot{O}$O) and D(R−OOH) strengthen with increasing methyl substitution at the α-carbon but remain constant with increasing carbon chain length. We recommend a new set of group additivity contributions for the estimation of enthalpies of formation and bond energies.

Introduction

One of the main developments in combustion research today is the implication of a shift from hydrocarbon fossil fuels to fuels derived from biomass, or biofuels, to mitigate climate change and to counteract the depletion of petroleum. As the principal components of plant matter are cellulose and starch, $(C_6H_{10}O_5)_n$, these new fuels will contain substantial amounts of oxygen that will have both positive and negative impacts on exhaust emissions: positive in reduction of particulate emissions; negative in increased propensity to form toxic byproducts such as aldehydes. A fundamental understanding of oxygenate, or biofuel, combustion chemistry is necessary to fully exploit the former and minimize the latter.

The current market leader, bioethanol, suffers from some disadvantages as an automotive fuel including too high a solubility in water, low energy density, high vapor pressure, *etc*. In addition, it appears that the wholesale replacement of gasoline by an ethanol−gasoline blend will degrade local air quality and result in increases in human health problems.[1] Recent work[2] has also shown that seepage of bioethanol into the water table exarcebates the existing difficulty posed by leaks of methyl *tert*-butyl ether (MTBE) from faulty underground storage tanks[3] and reduces the rates of biodegradation of spilt aromatics.[4] Note that MTBE rose from almost total obscurity to become one of the most produced organic compounds in the world because it was believed that it could simultaneously replace the lead compounds in gasoline *and* improve urban air quality. It has since been banned as a gasoline additive in some areas of the United States and is in the process of being replaced by ethanol elsewhere.[5]

The search is thus on for oxygenates that can be readily produced from biomass not destined for human consumption, perform well in engines and turbines and which will not unwittingly impact negatively on the environment; *n*-butanol is one such candidate.

Hence, as part of an ongoing study of the combustion chemistry of oxygenates in general and biobutanol, $CH_3(CH_2)_2$-CH_2OH, in particular, we have re-examined the thermochemistry of organic hydroperoxides, ROOH, for methyl, ethyl, *n*-propyl and *n*-butyl for which little data exist. Previous studies have largely focused on changing the alkyl group along the sequence R = methyl, ethyl, isopropyl and *tert*-butyl to determine the effect of increased substitution on bond energies. We have also included isobutyl and *sec*-butyl species to have a comprehensive overview of the thermochemistry of this set of compounds. Some of these hydroperoxides and their radicals play key roles in the chemistry of the atmosphere,[6–8] alkyl peroxy radicals are found in biological systems[9] and are a cause of concern in indoor environments.[10]

Alkylperoxy radicals play a key role in the oxidation of fuels at cool-flame temperatures and the competition between their isomerization to hydroperoxyalkyl radicals or dissociation is central to an understanding of combustion in novel internal combustion engines under active development.[11]

Computational Methods

The complete basis sets methods of Petersson et al.,[12,13] CBS-QB3 and CBS-APNO, have been used with the application Gaussian-03.[14] A particularly clear exposition of and a comparison of the achievable accuracies of these methods is given by Pokon et al.[15] They have shown that for gas-phase deprotonation reactions, typified by

$$CH_3NH_2 \rightarrow CH_3NH^- + H^+$$

root-mean-square deviations of 6.2 and 4.8 kJ mol $^{-1}$ in reaction enthalpies can be achieved in comparison to experiment for the two methods respectively. To improve upon the precision of these results, an isodesmic set of reactions has been used (a complete listing of reactions, energies and structures is available in the Supporting Information document) in this work in conjunction with reasonably well-established enthalpies of formation for a small set of reference compounds; the absence of imaginary frequencies indicated that all optimized structures were true minima. The CBS methods do of course operate under a set of well-known assumptions and neglect, for example,

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* To whom correspondence should be addressed. E-mail: john.simmie@nuigalway.ie.
[†] Combustion Chemistry Centre.
[‡] Department of Mathematics.

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anharmonic effects, internal rotors, etc. that do impact on the enthalpy, but these additional complications are seldom of concern in the first instance and are shared by the majority of electronic structures calculations in the literature today.

The general approach taken was to compute $\Delta Hf°(298.15K)$ for the first member of the sequence CH_3OOH and then to use this value (but not exclusively) to determine the next compound in the series and so on. As the molecular complexity increases, it becomes easier to frame suitable isodesmic reactions and therefore there is not an inevitable increase in the uncertainty with which formation enthalpies can be determined. The reaction enthalpies, ΔH_r, which do impact on the formation enthalpy of the target species, differed *at most* by 1.4 kJ mol^{-1} for QB3 and APNO calculations for ROOH and averaged |0.4| kJ mol^{-1}; even for the RO radicals the maximum difference only amounted to 1.9 kJ mol^{-1}. Over the 78 working reactions utilized in this work the precision of the computed reaction enthalpies is consistently high.

The model chemistries CBS-QB3 and CBS-APNO provide independent determinations of the true ΔH_r value for each reaction and hence the average of these gives an obvious (and statistically consistent) estimate of the true value that can be used in the subsequent calculations. Although no error estimates are available for the individual ΔH_r values, we can use the differences to obtain an error estimate for the average value. Under the assumption that the QB3 and APNO values are independent determinations, X and Y, of the true value, the error in the differences is the same as that of the sum, $\sigma(X - Y) = \sigma(X + Y)$, and the error for the average is half of this. Examination of the differences in QB3 and APNO values suggests that the assumption of constant variability is reasonable (there is only very weak dependence of the differences on the average value), and hence the sample variance, σ_d^2, of the set of difference values can be used to estimate this variability. We could now use $\sigma_d/2$ as the error estimate for the ΔH_r values in the subsequent overall error determination. However, to allow for possible slight dependence in these determinations, we in fact use $2\sigma_d$ or 1.6 kJ mol^{-1}—this provides us with a relatively conservative estimate of the overall error, rooted in the results obtained.

The enthalpy of formation of the target species, x_j, for isodesmic reaction j is computed algebraically together with an associated uncertainty of $u_j = (\sum u_i^2)^{1/2}$, where u_i are the uncertainties of the species and of the reaction enthalpy in the self-same isodesmic reaction. The final reported enthalpy is calculated via a weighted grand mean, $\bar{x} = \sum (x_j/u_j^2)/\sum(1/u_j^2)$, and the final uncertainty is given as $\bar{u} = 1/[\sum(1/u_j^2)]^{1/2}$.

This procedure discriminates against those isodesmic reactions that necessarily involve less well-defined reference species, such as reaction 5. The final calculated enthalpies of formation and their associated uncertainties are relatively insensitive to our assumed uncertainty in the computed reaction enthalpies. As a check on the validity of the results, atomization calculations have also been performed at the same levels of theory; the systematic discrepancies noted by Saeys et al.[16] for CBS-QB3 have been borne in mind, however.

A conformational study of 1-butanol by Ohno and co-workers[17] identified 14 possible conformational forms—their general findings we have subsequently confirmed at much higher levels of theory although the rank orders of energies are not identical. In the case of *n*-butyl hydroperoxide a conformer distribution calculation[18] at semiempirical, AM1, level highlights some 54 rotamers. A fully detailed study of all the rotamers of the more than 30 species in this work would therefore be highly laborious and probably counterproductive (see later discussion in this work and a recent study by Bond[19] that outlines the pitfalls associated with the computation of enthalpies for molecules with multiple conformations). Instead, care was taken to ensure that both theoretical methods computed the energy of nearly identical rotamers—a situation slightly complicated by the fact that the geometry optimization procedures are not the same in CBS-QB3, which employs B3LYP/6-311G(2d,d,2p), and in CBS-APNO where HF/6-311G(d,p) is followed by QCISD/6-311G(d,p).

Alkyl Hydroperoxides

Methyl Hydroperoxide, MeOOH. Methyl hydroperoxide, CH_3OOH, has been the subject of numerous publications[20–24] since a comprehensive review by Dorofeeva et al. in 2001.[25] They concluded that $\Delta H_f(298.15K) = -139.0 \pm 5.0$ kJ mol^{-1} represented the best estimate from values which ranged from −122 to −143 kJ mol^{-1}. The latter, however, seems to have been based on the assumption that reaction 2 is thermoneutral—this is in conflict with our calculations, which predict a reaction enthalpy of ≈−10.5 kJ mol^{-1}.

Subsequently, Blanksby and colleagues[20] reported a value of −129.3 kJ mol^{-1}, and Sheng et al.[21] computed −128.3 ± 5.1 from a series of working reactions, including reaction 1 below, at a high level of theory. Sumathi and Green[23] carried out CBS-Q atomization calculations for methyl, ethyl, isopropyl and *tert*-butyl hydroperoxides to derive group additivity values. Khursan and Antonovsky[22] computed a number of values from −120.1 to −133.4 kJ mol^{-1}, and most recently Matthews et al.[24] deduced values of −125.9 from experiment and −127.2 kJ mol^{-1} from CBS-APNO calculations. The situation is thus still unclear.

The following isodesmic reactions were chosen:

$$\mathrm{MeOOH + HOH = MeOH + HOOH} \tag{1}$$

$$\mathrm{MeOOH + MeOMe = MeOH + MeOOMe} \tag{2}$$

$$\mathrm{2MeOOH = MeOOMe + HOOH} \tag{3}$$

with reaction 3 almost thermoneutral, $\Delta H_r = -1.4$ and −0.7 kJ mol^{-1} at both QB3 and APNO levels of theory. The calculations are based on well-established formation enthalpies for water[26] of −241.83 ± 0.04, methanol[27] of −201.2 ± 0.21, dimethyl ether[28] of −184.1 ± 0.5 and hydrogen peroxide[29] of −135.8 ± 0.17 kJ mol^{-1} respectively. The somewhat less well-known value for dimethyl peroxide[25] of −125.5 ± 5.0 is also required. The results for all three isodesmic reactions at two levels of theory, Table 1, show that ΔH_f for MeOOH is −129.5 ± 0.9 kJ mol^{-1} at the 95% level of confidence. This is in good agreement with the Blanksby et al.[20] CBS-APNO result of −129.3 kJ mol^{-1}.

Ethyl Hydroperoxide, EtOOH. In the case of ethyl hydroperoxide there is no consensus. A bomb calorimeter result[30,31] ΔH_f(EtOOH) of −200 kcal mol^{-1} carries a very large error of ±50 kJ mol^{-1} whereas an isodesmic calculation[32] at QCISD(T)/6-311G**//MP2(full)/6-31G* level of

$$\mathrm{EtOO^{\cdot} + MeOOH = EtOOH + MeOO^{\cdot}}$$

gives −166.9 kJ mol^{-1}. Later computations by Sheng et al.[21] at CBS-Q reported −166.9 ± 6.7 kJ mol^{-1} from a consideration of reaction 4, but this was based on ΔH_f(MeOOH) = −133.1 kJ mol^{-1}; if the current value of −129.5 is used instead, then ΔH_f(EtOOH) = −163.3 kJ mol^{-1}.

Here, insofar as possible, the same set of reference species have been chosen in isodesmic reactions for ethyl hydroperoxide

TABLE 1: Enthalpies of Formation of ROOH and RO at 298.15 K (kJ/mol)

	isodesmic reactions							atomization	
species	QB3			APNO			mean	QB3	APNO
MeOOH	−129.3	−131.4	−130.0	−128.8	−132.4	−130.3	−129.5 ± 0.9	−134.5	−129.3
EtOOH	−163.9	−165.9	−163.7	−163.6	−166.5	−162.9	−163.7 ± 0.9	−166.8	−164.8
nPrOOH	−183.8	−183.9		−183.4	−182.7		−183.4 ± 1.1	−185.2	−187.3
iPrOOH	−200.6	−200.6	−200.2	−200.6	−199.8	−200.6	−200.4 ± 0.9	−203.8	−206.2
nBuOOH	−202.4	−202.8		−202.7	−201.9		−202.4 ± 1.0	−205.0	−210.8
tBuOOH	−239.6	−240.1	−239.7	−239.5	−238.7	−239.2	−239.5 ± 0.9	−242.5	−247.9
iBuOOH	−210.5	−209.6	−210.5	−210.4	−208.5	−210.7	−210.0 ± 0.9	−212.6	−218.1
sBuOOH	−221.0	−220.1	−219.9	−221.2	−219.3	−219.9	−220.3 ± 0.9	−223.1	−228.9
$MeOO^{\cdot}$	+12.3	+12.1		+12.5	+11.8		+12.2 ± 0.9	+8.1	+8.6
$EtOO^{\cdot}$	−23.8	−23.7	−23.7	−23.3	−23.7	−23.0	−23.5 ± 0.7	−26.0	−28.3
$nPrOO^{\cdot}$	−44.2	−44.4		−44.2	−43.7		−44.1 ± 1.1	−44.7	−51.7
$iPrOO^{\cdot}$	−62.4	−62.6	−62.3	−62.4	−61.8	−62.3	−62.3 ± 0.9	−64.8	−71.6
$nBuOO^{\cdot}$	−63.0	−63.3		−62.8	−62.3		−62.8 ± 1.0	−64.5	−74.6
$tBuOO^{\cdot}$	−103.8	−104.3	−104.0	−102.9	−102.4	−102.8	−103.3 ± 0.8	−105.7	−114.9
$iBuOO^{\cdot}$	−70.7	−71.2	−70.8	−70.8	−70.3	−70.7	−70.7 ± 1.0	−71.8	−81.9
$sBuOO^{\cdot}$	−82.5	−83.0	−82.6	−82.6	−82.1	−82.6	−82.6 ± 1.1	−84.9	−95.1

as for MeOOH except for ethanol whose enthalpy of formation[27] is taken as −235.2 ± 0.5 kJ mol^{-1}:

$$\mathrm{EtOOH + MeOH = EtOH + MeOOH} \tag{4}$$

$$\mathrm{EtOOH + MeOMe = EtOH + MeOOMe} \tag{5}$$

$$\mathrm{EtOOH + HOH = EtOH + HOOH} \tag{6}$$

As before, the agreement between the final isodesmic result of −163.7 ± 0.9 kJ mol^{-1} and atomization computations is very good; this is also in excellent agreement with the −165.3 kJ mol^{-1} of Blanksby et al.[20] and the corrected Sheng et al.[21] result of −163.3 kJ mol^{-1}.

Propyl Hydroperoxides, nPrOOH and iPrOOH. The isodesmic reaction:

$$\mathrm{nPrOO + EtOH = nPrOH + EtOOH}$$

conserves not just bond types but also neighboring interactions as well (isogeitonic[33]) and hence is almost thermoneutral. Together with ΔH_f(nPrOH) = −255.2 ± 1.3[34] and in conjunction with a second isodesmic reaction:

$$\mathrm{nPrOO + HOH = nPrOH + HOOH}$$

a result of −183.4 ± 1.1 kJ mol^{-1} is obtained. This is in excellent agreement with the −184.3 ± 0.6 of Sebbar et al.[35] but not with an earlier result[36] of −187.3 ± 1.7 kJ mol^{-1}.

A similar strategy was employed for the isopropyl hydroperoxide—our value of −200.4 ± 0.9 kJ mol^{-1} neatly brackets two earlier determinations of −194.6 and −205.0 kJ mol^{-1}, respectively.[32,37]

Butyl Hydroperoxides, *x*BuOOH. As before, consideration of the isogeitonic and essentially thermoneutral reaction:

$$\mathrm{nBuOOH + nProH = nBuOH + nPrOOH}$$

yields −202.4 and −202.7 kJ mol^{-1} based on a ΔH_f(nBuOH) of −274.9 ± 0.6 kJ mol^{-1} at QB3 and APNO levels, respectively.[34] The final averaged value corresponds to −202.4 ± 1.0 kJ mol^{-1} when a second working reaction, analogous to eq 6, is included.

There is a distinct lack of previous data for this species and its radical, but very recently Zhu et al.[38] have computed a CBS-QB3 value of −208.1 kJ mol^{-1} from the isodesmic reaction

$$\mathrm{nBuOOH + nPrH = nPrOOH + nBuH}$$

They used a reference value of ΔHf°(nPrOOH) of −187.3 from Chen and Bozzelli;[36] if this is corrected to reflect the value found for *n*-propyl hydroperoxide in this work, then ΔHf°(nBuOOH) = −204.3 kJ mol^{-1}, which is in very good agreement with our result of −202.4 ± 1.0 kJ mol^{-1}.

A similar set of reactions for *tert*-butyl hydroperoxide, $(CH_3)_3COOH$, is augmented by the direct comparison:

$$\mathrm{tBuOOH + nBuOH = tBuOH + nBuOOH}$$

where a ΔH_f(tBuOH) of −312.6 ± 0.9 kJ mol^{-1} was used.[39] In a similar vein, values for both $C_2H_5CH(OOH)CH_3$, *sec*-butyl hydroperoxide or sBuOOH and $(CH_3)_2CHCH_2OOH$ isobutyl hydroperoxide or iBuOOH were computed via ΔH_f(sBuOH) = −292.7 ± 1.5 kJ mol^{-1} and ΔH_f(iBuOH) = −283.8 ± 0.9 kJ mol^{-1}.[40,41]

Note that the APNO atomization values diverge more and more from the isodesmic results as one increases the number of carbon and hydrogen atoms (Sumathi and Green[42] have noted that *tert*-butyl systems are systematically overestimated at the CBS-Q level). This is in line with the observations of Saeys et al.[16] who eliminated similar deviations in their CBS-QB3 atomization computations of the enthalpies of formation of alkyl radicals by modifying the atomic enthalpies of both carbon and hydrogen by −1.29 kJ mol^{-1} per C-atom and −0.28 kJ mol^{-1} per H-atom. These systematic corrections were designed to allow for core-valence correlation and scalar relativistic effects that the complete basis sets method neglects. Clearly this approach is of limited utility as the number of different elements increases and is not pursued here.

Alkyl Peroxy Radicals. In the case of the peroxy radicals, RO, the well-established[29] value for hydroperoxy of +12.3 ± 0.3 kJ mol^{-1} has been used as a reference in reaction 7, and the result checked with eq 8.

$$\mathrm{MeOO^{\cdot} + HOH = MeOH + HOO^{\cdot}} \tag{7}$$

$$\mathrm{MeOO^{\cdot} + HOOH = MeOOH + HOO^{\cdot}} \tag{8}$$

There is good agreement with semiempirical PM3 calculations by Shallcross et al.[6] for methyl peroxy of 12.5 kJ mol^{-1}, but this is almost certainly fortuitous, as their values for the higher alkyl peroxy radicals are in considerable disagreement with ours.

Very recent energy-resolved photoionization experiments on alkylperoxy radicals by Meloni et al.[43] led to an enthalpy of formation of MeO of 22.4 ± 5 kJ mol^{-1} at 0 K, which implies 12.4 ± 5 at 298.15 K; this is in excellent agreement with our weight-averaged isodesmic result of +12.2 ± 0.9 kJ mol^{-1}, Table 1.

TABLE 2: Results for ROOH and RO$\dot{\mathrm{O}}$, Δ*H*f°(298.15K) (kJ mol^{-1})

species	this work	literature
MeOOH	−129.5 ± 0.9	−125.3,[37] −125.9 ± 4.2,[24] −139.0 ± 5.0,[25] −128.7,[23] −133.4,[42] −131.2 ± 3.4,[35] −133.1[32]
EtOOH	−163.7 ± 0.9	−158.9,[37] −200 ± 50,[30] −164.7,[21] −165.3 ± 2.9,[20] −162.3,[23] −164.3 ± 0.1,[35] −166.9[32]
nPrOOH	−183.4 ± 1.1	−184.3 ± 0.6,[35] −187.3 ± 1.7[57]
iPrOOH	−200.4 ± 0.9	−194.6,[37] −205.0[32,57]
nBuOOH	−202.4 ± 1.0	−208.1[38]
tBuOOH	−239.5 ± 0.9	−237.2,[37] −245.1,[22] −242.3 ± 2.0,[57] −244.3[32]
iBuOOH	−210.0 ± 0.9	
sBuOOH	−220.3 ± 0.9	
$MeOO^{\cdot}$	+12.2 ± 0.9	+14.2,[37] +12.4 ± 5,[43] 9.0,[56] 12.5,[6] +20.1 ± 5.0,[20] +8.5 ± 0.4[35]
$EtOO^{\cdot}$	−23.5 ± 0.7	−20.5,[37] −28.5 ± 9.6,[20] −27.4 ± 9.9,[56] −9.6,[6] −24.1 ± 0.4[35]
$nPrOO^{\cdot}$	−44.1 ± 1.1	−50.6[58]
$iPrOO^{\cdot}$	−62.3 ± 0.9	−59.7,[37] −36.8[6]
$nBuOO^{\cdot}$	−62.8 ± 1.0	−71.7[38]
$tBuOO^{\cdot}$	−103.3 ± 0.8	−103.2,[37] −61.7,[6] −105.3[32]
$iBuOO^{\cdot}$	−70.7 ± 1.0	
$sBuOO^{\cdot}$	−82.6 ± 1.1	

TABLE 3: Recommended Group Contributions

group	ΔH_f(298K)/kJ mol $^{-1}$
$C/C_2/H_2$	−19.37
$C/C_3/H$	−5.02
$C/C/H_2/OO$	−30.96
$C/C_2/H/OO$	−24.69
$C/C_3/OO$	−23.05
OO/C/H	−90.79

TABLE 4: Results for R$\dot{\mathrm{O}}$, Δ*H*f°(298.15K) (kJ mol^{-1})

species	this work	literature
$MeO^{\cdot}$		+21.0 ± 2.1[47]
$EtO^{\cdot}$	−13.0 ± 1.3	−15.1 ± 3.3,[59] −13.6 ± 3.3[47]
$nPrO^{\cdot}$	−33.1 ± 1.4	−30.1 ± 8.4[34]
$iPrO^{\cdot}$	−43.9 ± 1.2	−48.3 ± 2.8[59]
$nBuO^{\cdot}$	−49.8 ± 1.3	−56.4[34]
$tBuO^{\cdot}$	−83.3 ± 1.3	−85.6 ± 2.9,[59] −86.9[34]
$iBuO^{\cdot}$	−61.2 ± 1.3	−65.1[34]
$sBuO^{\cdot}$	−61.9 ± 1.3	−69.8[34]

TABLE 5: ROO−H Bond Dissociation Energies (kJ mol $^{-1}$) (a) from Formation Enthalpies and (b) and (c) Directly via QB3 and APNO, Respectively

	this work	literature		
species	(a)	(b)	(c)	
MeOO−H	360 ± 1	361	356	370 ± 2,[60] 365,[61] 358[62]
EtOO−H	358 ± 1	359	355	355 ± 9,[20] 363[61]
nPrOO−H	357 ± 2	358	354	335[63]
iPrOO−H	356 ± 1	357	353	356,[61] 352[20]
nBuOO−H	358 ± 1	359	354	
tBuOO−H	354 ± 1	355	351	344,[61] 374[64]
iBuOO−H	357 ± 1	359	354	
sBuOO−H	356 ± 1	356	352	

As before, a set of reactions

$$\mathrm{EtOO^{\cdot} + MeOH = EtOH + MeOO^{\cdot}} \tag{9}$$

$$\mathrm{EtOO^{\cdot} + HOOH = EtOOH + HOO^{\cdot}} \tag{10}$$

$$\mathrm{EtOO^{\cdot} + HOH = EtOH + HOO^{\cdot}} \tag{11}$$

was chosen to minimize the electronic and structural differences of the products from the reactants. The final result of −23.5 ± 0.7 kJ mol $^{-1}$ is higher than the atomization values.

Merle and co-workers[44] have carried out a comprehensive CBS-QB3 study of the *n*-propylperoxy radical and report that five different rotamers (gG, tG, gT, gG′, and tT according to the orientation about the O−O−C−C and O−C−C−C dihedrals) exist, all of which are present in significant concentrations, 28:26:20:14:12, at room temperature and in thermal equilibrium. A population-weighted average of their computed enthalpies lies close to the individual value for the gT rotamer; we have used the gT rotamer as a representative *n*-propylperoxy radical to reduce the arithmetic burden of treating each isomer as a separate species. Because the experimental enthalpy itself corresponds to a weighted average of the actual enthalpies for each rotamer *i*, with mole fraction x_i (given that the rotational barriers are small):

$$\Delta H_f(\text{exptl}) = \sum_{i=1}^{n} \{x_i \Delta H_f(i)\}$$

this is not an unreasonable assumption.

An overview of the conformers of methyl, ethyl, propyl and butyl peroxy radicals has been given by Glover and Miller[45] who show that 14 conformers are expected for nBuO, 9 for sBuO, 5 for iBuO, and 1 for tBuO, whereas EtO and iPrO have 2 and MeO just 1.

Appropriate variations of reactions 9 and 11 were used for both the propoxy radicals together with the direct comparison:

$$\mathrm{iPrOO^{\cdot} + nPrOH = iPrOH + nPrOO^{\cdot}}$$

to estimate their enthalpies of formation. Exactly the same approach was used for the four butyl radicals.

Very recently, Zhu et al.[38] have computed a CBS-QB3 value of −71.7 kJ mol^{-1} from the isodesmic reaction:

$$\mathrm{nBuOO^{\cdot} + nPrH = nPrOO^{\cdot} + nBuH}$$

for the nBuO radical. They used a reference value of Δ*H*f°(nPrO) of −50.6 kJ mol^{-1} from Chen and Bozzelli;[36] if this is corrected to reflect the value found for the radical in this work, then Δ*H*f°(nBuO$\dot{\mathrm{O}}$) = −65.2 kJ mol^{-1}, which is in better agreement with our result of −62.8 ± 1.0 kJ mol^{-1}.

A summary of all our results for ROOH and RO and comparisons with a selection of the best literature values are given in Table 2. The agreement with group additivity estimates[46] is very good for methyl, ethyl, isopropyl and *tert*-butyl hydroperoxides but not as good for the other members. We have used our own data to generate a new set of recommended group values, Table 3, which are to be used in conjunction with the derived bond energies of *D*(ROO−H) = 357.3 and *D*(RO−H)

TABLE 6: RO−OH Bond Dissociation Energies (kJ mol $^{-1}$) (a) from Formation Enthalpies and (b) and (c) Directly via QB3 and APNO, Respectively

	this work	literature		
species	(a)	(b)	(c)	
MeO−OH	188 ± 2	191	187	191,[51] 189 ± 4,[65] 195 ± 6[66]
EtO−OH	188 ± 2	191	186	194,[51] 179 ± 6[65]
nPrO−OH	188 ± 2	191	187	
iPrO−OH	194 ± 2	197	192	195,[51] 186 ± 6[65]
nBuO−OH	190 ± 2	191	189	
tBuO−OH	193 ± 2	197	192	196,[51] 180 ± 2[67]
iBuO−OH	186 ± 2	190	185	
sBuO−OH	196 ± 2	198	194	

TABLE 7: R−OȮ Bond Dissociation Energies (kJ mol $^{-1}$) (a) from Formation Enthalpies and (b) and (c) Directly via QB3 and APNO, Respectively

	this work	literature	
species	(a)	(b)	(c)
MeO−O$^{\cdot}$	258 ± 2	260	259
EtO−O$^{\cdot}$	260 ± 2	261	260
nPrO−O$^{\cdot}$	260 ± 2	261	262
iPrO−O$^{\cdot}$	268 ± 2	270	268
nBuO−O$^{\cdot}$	262 ± 2	262	263
tBuO−O$^{\cdot}$	269 ± 2	272	269
iBuO−O$^{\cdot}$	259 ± 2	261	260
sBuO−O$^{\cdot}$	270 ± 2	272	271

TABLE 8: Assumed Enthalpies (kJ mol^{-1}) for Reference Alkyl Radicals[32]

species	$\Delta Hf°$(298.15K)	species	$\Delta Hf°$(298.15K)
Me	146.7 ± 0.3	nBu	81.8 ± 4.0
Et	119.7 ± 0.7	tBu	55.0 ± 3.0
nPr	101.3 ± 1	iBu	73.8 ± 4.0
iPr	90.2 ± 2	sBu	70.2 ± 2.1

TABLE 9: R−OȮ Bond Dissociation Energies (kJ mol $^{-1}$) (a) from Formation Enthalpies and (b) and (c) Directly via QB3 and APNO, Respectively

	this work	literature		
species	(a)	(b)	(c)	
Me−OO$^{\cdot}$	134 ± 1	139	138	137 ± 4,[56] 135,[53] 138[44]
Et−OO$^{\cdot}$	143 ± 1	146	148	149 ± 8,[56] 130 ± 5,[68] 148[44]
nPr−OO$^{\cdot}$	145 ± 2	146	153	151[44]
iPr−OO$^{\cdot}$	152 ± 3	155	162	155 ± 10,[56] 135 ± 5,[68] 157[44]
nBu−OO$^{\cdot}$	145 ± 4	146	156	
tBu−OO$^{\cdot}$	158 ± 3	161	170	153 ± 7,[56] 126 ± 5[64]
iBu−OO$^{\cdot}$	145 ± 4	146	156	
sBu−OO$^{\cdot}$	153 ± 2	155	165	

= 440.0 kJ mol^{-1} for alkylperoxy and alkoxy radicals, respectively.

Alkoxy Radicals. In view of the paucity of consistent and reliable data for the lower alkoxides, R, required for the computation of bond dissociation energies (see below), a series of isodesmic reactions were constructed on the basis of principles similar to those outlined above and using the Ruscic et al.[47] value for methoxy of +21.0 ± 2.1 kJ mol^{-1} to "anchor" the calculations. The results, Table 4, are in moderate agreement with literature values; if a lower value of 17.2 kJ mol^{-1} is adopted,[48] then all the values in Table 4 are lowered in energy by ≈4 kJ mol^{-1}. However, the higher value for Me seems to be reliable because for

$$\text{MeO}^{\cdot} + \text{HOH} = \text{MeOH} + \text{HO}^{\cdot}$$

an average reaction enthalpy of 57.4 kJ mol^{-1} from both model chemistries yields $\Delta H_f(\text{Me}\dot{\text{O}}) = 20.6 \pm 1.2$ kJ mol^{-1}.

Bond Dissociation Energies. Recent authoritative compilations of bond dissociation energies[49,50] carry the recommendations $D(\text{MeOO}-\text{H}) = 370 \pm 2$ and $D(\text{EtOO}-\text{H}) = 355 \pm 9$ kJ mol^{-1} largely based on experimental determinations; there are no comparable values for the *n*-propyl or *n*-butyl hydroperoxides although $D(\text{ROO}-\text{H})$ for R = isopropyl is given as 356 and for R = *tert*-butyl as 344−374.

Using the above values in Table 1 together with $\Delta Hf°(\dot{\text{H}}) = 218.0$ kJ mol^{-1} we can show that $D(\text{ROO}-\text{H})$ is essentially independent of R from Me through to Bu and that 357 ± 3 summarizes our results, Table 5, where columns b and c are directly calculated as follows from the CBS-X enthalpies, *H*:

$$D(\text{ROO}-\text{H}) = H(\text{ROO}^{\cdot}) + H(^{\cdot}\text{H}) - H(\text{ROOH})$$

There is very good agreement between the isodesmic results and the QB3 ones; the APNO are some 4−5 kJ mol^{-1} weaker. There is a slight weakening of the bond energy with increasing methyl substitution at the α-carbon from 360 → 358 → 356 → 354 kJ mol^{-1}.

Much the same conclusion applies to the O−O bond strengths for the *n*-alkyls that have an effectively constant value of ≈190 kJ mol^{-1}, Table 6. The results in column a depend upon the enthalpies of formation of hydroxyl (taken as 37.36 ± 0.13 kJ mol^{-1})[29] and the alkoxy radicals, Table 4.

It appears from the direct calculations, columns b and c in Table 6, that the branched alkyls exhibit slightly stronger O−O bond strengths—in line with the CBS-QB3 findings of Wijaya et al.[51]—although the calculations in column a, based on our isodesmic enthalpies for ROOH, are more ambiguous.

In reality, the nature of the alkyl moiety has very little effect on the O−O bond strength and a constant value of 190 kJ mol^{-1} would summarize these results. Khursan et al.[52] reached the same conclusion RO−OH = 193 ± 3 kJ mol^{-1}, for the series methyl → *tert*-butyl, via isodesmic reactions at RHF/3-21G.

The O−O bond energies in the peroxy radicals are also essentially constant, Table 7, at ca. 262 kJ mol^{-1}. The directly computed QB3 and APNO values are in very good agreement with each other and agree quite well with most of the derived values.

The alkyl−O bond energies are of significance to biology and medicine not least because in the auto-oxidation of polyunsaturated fatty acids an H-atom transfer to a peroxy radical occurs.[53] We have used literature values for the alkyl radicals, Table 8, in conjunction with our isodesmic averages for RO, and also used a more direct approach

$$D(\text{R}-\text{OO}^{\cdot}) = H(\text{R}^{\cdot}) + \text{H}(\text{O}_2) - H(\text{ROO}^{\cdot})$$

employing the CBS-X enthalpies, *H*, at 298.15 K, to compute the bond dissociation energies, Table 9.

All three values show a pleasing degree of consistency. Increasing methyl substitution at the α-carbon strengthens the $\text{C}-\dot{\text{O}}_2$ bond from 134 → 143 → 152 to 158 kJ mol^{-1}, but increasing the normal carbon chain length from $\text{CH}_3\text{CH}_2\dot{\text{O}}\text{O}$ onward has little effect on the bond strength. This is in conflict with the results of Kranenburg et al.[54] who reported that $D(\text{R}-\text{O})$ is not sensitive to substitution by alkyl groups. The *sec*-butyl BDE is the same as that for isopropyl and the isobutyl value is the same as for the normal isomers. These conclusions are in concordance with current views of hyperconjugation stabilizing the resultant carbon-centered radical and thus weakening the C−X bond.[55]

TABLE 10: R−OOH Bond Dissociation Energies (kJ mol^{-1}) (a) from Formation Enthalpies and (b) and (c) Directly via QB3 and APNO, Respectively

	this work	literature		
species	(a)	(b)	(c)	
Me−OOH	288 ± 1	293	286	300.4 ± 12.6[65]
Et−OOH	296 ± 1	301	294	332.2 ± 20.9[65]
nPr−OOH	297 ± 2	302	295	364.4,[65]
iPr−OOH	303 ± 3	308	301	298.3,[65]
nBu−OOH	297 ± 4	302	295	
tBu−OOH	307 ± 3	312	304	309.2 ± 4.2[65]
iBu−OOH	296 ± 4	303	296	
sBu−OOH	303 ± 2	309	302	

For *D*(Me−O) there is satisfactory agreement between the reanalyzed value due to Knyazev and Slagle[56] and the G3MP2 calculations of Pratt et al.[53] In other cases the uncertainties in the literature values are so large that it is more difficult to come to any firm conclusion except that there is good agreement with the Knyazev and Slagle values and, not unexpectedly, with CBS-QB3 computations by Merle et al.[44]

Finally the alkyl−OOH bond energies have been computed as before, Table 10, with the alkyl formation enthalpies taken from Table 8 and our results for ROOH to yield column a and the direct computations from the reported CBS enthalpies at 298.15 K in columns b and c. Literature values are not only scarce but are quite uncertain and seemingly inconsistent. We note that our values indicate a strengthening of the C−OOH bond with increasing methyl substitution at the α-carbon, 288 → 296 → 303 → 307, whereas lengthening the carbon chain does not affect the bond energy. APNO calculations underestimate the bond energy by some 7 kJ mol^{-1} compared to QB3 but their mean are in excellent agreement with the isodesmic results.

Conclusions

An internally consistent set of formation enthalpies for alkyl hydroperoxides and alkyl peroxy radicals have been computed for methyl through butyl. The resultant values are in good agreement with the very small number of recent high-quality experiments.

The isodesmic reactions chosen in this evaluation render the computational expense of the CBS-APNO methodology unnecessary; the CBS-QB3 procedure is able to deliver highly satisfactory results at a fraction of the calculational cost (*ca.* 15 times faster). The atomization method produces reasonable bond dissociation energies but is not sufficiently reliable in the computation of enthalpies of formation; however, this procedure is still of value in determining inconsistencies in the enthalpies of formation of those compounds used as reference species.

Bond dissociation energies derived from these and other well-established enthalpies present a clear and coherent picture; in the case of the hydroperoxides the O−H and O−O energies do not depend upon the nature of the alkyl group. In contrast, the R−O_2H, RO−O and the R−O_2 bond energies increase with increasing methyl substitution at the α-carbon.

This work provides a useful starting platform for future efforts on larger systems where such high-level methods will not be appropriate.

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Supporting Information Available: Tables of CBS enthalpies and isodesmic reactions. Chemical structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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