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Assessing thermochemical data

John L. Holmes [a,*], Christiane Aubry [a], Xian Wang [b]

[a] *Chemistry Department, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada*
[b] *College of Chemistry and Material Science, South-Central University for Nationalities, Wuhan, PR China, 430074*

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Abstract

This paper describes, with examples, a critical assessment of thermochemical data for some small molecules and free radicals. The available heats of formation, $\Delta_f H^\circ$ (all 298 K values). for simple alkyl hydroperoxides and di-alkyl peroxides were compared and new data are provided. The $\Delta_f H^\circ$ values, all ±5 kJ/mol, are: CH_3OOH, −135; CH_3CH_2OOH, −168; *n*-C_3H_7OOH, −189; *s*-C_3H_7OOH, −205; *t*-C_4H_9OOH, −240; CH_3OOCH_3, −132; $CH_3CH_2OOCH_3$, −165; $C_2H_5OOC_2H_5$, −198; *n*-C_3H_7OO*n*-C_3H_7, −240; *s*-C_3H_7OO*s*-C_3H_7, −272; *t*-C_4H_9OO*t*-C_4H_9, −342. These are consistent with established O–O bond dissociation energies and with additivity considerations. $\Delta_f H^\circ$ values for the corresponding alkoxy radicals are also addressed.

A similar survey was applied to the homologous *n*-alkyl aldehydes, C2 to C8, for which recommended $\Delta_f H^\circ$ values, all ±1.5 kJ/mol, are: −166.5, −189, −207.5, −227, −248, −268 and −289, respectively. Particular attention was given to $\Delta_f H^\circ(CH_3CO^\bullet) = -10.3 \pm 1.8$ kJ/mol.

The current NIST WebBook datum, $\Delta_f H^\circ(CS) = 280.3$ kJ/mol, is arguably the best value, being consistent with related thermochemical data.

Finally the $\Delta_f H^\circ$ values for the allylic free radicals ${}^\bullet CH_2CHCH_2$, 174 ± 3 kJ/mol, $CH_2CHCH^\bullet(OH)$, 4.5 ± 4 kJ/mol, and $(CH_2CH)_2{}^\bullet C(OH)$, 37 ± 4 kJ/mol, derived from experimental data and results of computational chemistry are described, together with some related homolytic bond strengths.

Keywords: Hydroperoxides; Peroxides; Aldehydes; Bond strengths

1. Introduction

Sharon Lias' name will always be associated with the thermochemistry of ions and neutral molecules as well as with their related properties such as proton and electron affinities. Much of her work is to be found in data collections, such as the NIST Chemistry WebBook and the many *Journal of Physical Chemistry Reference Data* publications that bear her name. A recent endeavour by two of us [1] brought us face-to-face with a number of surprising uncertainties and/or inconsistencies in the thermochemistry of simple neutrals and ions and the major part of this paper describes some typical examples and the solutions that we devised. It is intended also to provide some general guidelines for scientists who wish critically to assess thermochemical data.

First, it cannot be too strongly emphasised that a thermochemical datum is not an isolated number but rather should be viewed as part of a cycle in which the contributing entities are intimately interrelated. Therefore, the effect of changing only one datum for an ion or a molecule has a number of consequences. Consider the simple thermochemical cycle shown below:

$$\begin{tikzcd}
\mathbf{AB} \arrow[r, "\mathbf{D(AB)}"] \arrow[d, "\mathbf{IE(AB)}"'] & \mathbf{A^\bullet + B^\bullet} \arrow[d, "\mathbf{IE(A^\bullet)}"] \\
\mathbf{AB^{+\bullet}} \arrow[r, "\mathbf{D(AB^{+\bullet})}"] & \mathbf{A^+ + B^\bullet}
\end{tikzcd}$$

In this cycle, given that

$$D(AB) = \Delta_f H^\circ(A^\bullet) + \Delta_f H^\circ(B^\bullet) - \Delta_f H^\circ(AB)$$

$$D(AB^{\bullet+}) = \Delta_f H^\circ(A^+) + \Delta_f H^\circ(B^\bullet) - \Delta_f H^\circ(AB^{\bullet+})$$

and

$$\Delta_f H^\circ(AB^{\bullet+}) = IE(AB^{\bullet+}) + \Delta_f H^\circ(AB)$$

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[*] Corresponding author. Tel.: +1 613 562 5118; fax: +1 613 562 5170.
E-mail address: jholmes@science.uottawa.ca (J.L. Holmes).

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Table 1
Thermochemical data for ROOH and ROOR molecules

Molecule	$\Delta_f H^\circ$ (kJ/mol)		D(RO-OX)[a] (kJ/mol)	Recommended $\Delta_f H^\circ \pm 5$ (this work, kJ/mol)
	NIST[b]	Pedley[c]		
CH_3OOH	−131		193 ± 6	−135
CH_3CH_2OOH	−210	−199	191 ± 9	−168
n-C_3H_7OOH	−250		196 ± 13	−189
s-C_3H_7OOH	−197		198 ± 8	−205
t-C_4H_9OOH	−235		191 ± 9	−240
	−246 ± 5	−246 ± 5		
CH_3OOCH_3	−126 ± 1	−126 ± 1	174 ± 7	−132
$CH_3OOC_2H_5$	−197		172 ± 9	−165
$C_2H_5OOC_2H_5$	−193	−193 ± 2.5	170 ± 13	−198
	−200			
	−280			
n-$C_3H_7OO$$n$-$C_3H_7$			180 ± 16	−240
s-$C_3H_7OO$$s$-$C_3H_7$			174 ± 11	−272
t-$C_4H_9OO$$t$-$C_4H_9$	−343	−349 ± 3	170 ± 13	−342
	−341			

[a] Using the most recently evaluated $\Delta_f H^\circ$ data for the free radicals: $\Delta_f H^\circ(CH_3CH_2O^\bullet) = -14 \pm 4$ kJ/mol [4], $\Delta_f H^\circ(n\text{-}C_3H_7O^\bullet) = -30 \pm 8$ kJ/mol, $\Delta_f H^\circ(s\text{-}C_3H_7O^\bullet) = -49 \pm 3$ kJ/mol [5] and $\Delta_f H^\circ(HO^\bullet) = 37 \pm 0.3$ kJ/mol [4].

[b] Ref. [2].

[c] Ref. [6].

$$\Delta_f H^\circ(A^\bullet) = IE(AB^\bullet) + \Delta_f H^\circ(A^\bullet)$$

it follows that

$$D[AB] + IE[A^\bullet] = D[AB^{\bullet+}] + IE[M]$$

If the heat of formation value of any of the entities in the equations is changed or the ionization energies are revised, then necessarily the other numbers must be open to revision too. The typical examples given below are focused on neutral heats of formation, $\Delta_f H^\circ(298)$ values, and they have all been prompted by a need to review the currently available data.

2. Heats of formation and homolytic bond strengths of small organic molecules and free radicals

2.1. Alkyl hydroperoxides and dialkyl peroxides

The need for a reliable value for $\Delta_f H^\circ(CH_3CH_2OOH)$ stemmed from our re-evaluation of the available thermochemical data for the ion $^+CH_2OOH$ which can be generated by electronic ionization induced dissociation of CH_3CH_2OOH [1]. The NIST tables [2] give $\Delta_f H^\circ(CH_3CH_2OOH) = -210$ kJ/mol, a value that by itself appears to be not unreasonable. However, when compared with data for its homolgues, the −210 kJ/mol appears to be incompatible with $\Delta_f H^\circ(CH_3OOH) = -131$ kJ/mol [2], $\Delta_f H^\circ(s\text{-}C_3H_7OOH) = -197$ kJ/mol and $\Delta_f H^\circ(t\text{-}C_4H_9OOH) = -235$ (or −246) kJ/mol [2]. These objections arise from the premise that going from CH_3O–R to CH_3CH_2O–R results in the lowering of the heat of formation by some 33 ± 1 kJ/mol, as is shown by the analogous alkanols, ethers, esters, etc. [2], where CH_2 is being inserted between a saturated carbon centre and a hetero-atom (note that this does not apply when the CH_2 is inserted between C-atoms in aldehydes and carboxylic acids, e.g., CH_3COOH to CH_3CH_2COOH). Also, going from CH_3OR to s-C_3H_7O–R and to t-C_4H_9O–R reduces the heat of formation by about 70 ± 2 (based on data from NIST [2] for CH_3OH and $(CH_3)_2CHOH$ and CH_3OCH_3 and $CH_3OCH(CH_3)_2$) and 105 ± 6 kJ/mol, respectively. $\Delta_f H^\circ$ data for these series are highly reliable and have formed the basis for many thermochemical additivity terms [3] and therefore strongly suggest that the −210 kJ/mol [2] value for $\Delta_f H^\circ(C_2H_5OOH)$ should be reconsidered (Table 1).

Accordingly, all of the available thermochemical data for alkyl peroxy compounds were collated and compared for their consistency. Table 1 shows the available reference data for alkyl hydroperoxides and dialkyl peroxides taken from NIST [2] and the Pedley et al. collection [6].

The molecules are all homologues or simple isomers thereof, and so by the principle of additivity, the changes in going from, e.g., CH_3OX to C_2H_5OX to s-C_3H_7OX should be the same for all analogues of X, e.g., ethers, alkanols, esters, free radicals, etc., for which reliable data are certainly available. For the hydroperoxides and the alkyl peroxides the data were anchored to the average values for the t-C_4H_9– species. The last column gives our recommended value for $\Delta_f H^\circ$.

The recent book by Luo [7] gives the O–O bond strengths for the above dialkyl peroxides and these are significantly lower than those in the above table by about 10–15 kJ/mol. The discrepancies arise from the changes that have arisen in the radical $\Delta_f H^\circ$ values. From the above results it appears that $\Delta_f H^\circ(n\text{-}C_3H_7O^\bullet)$ may be too low by about 5 kJ/mol, to be in keeping with the enthalpy changes for CH_3CH_2O– to n-C_3H_7O– ($\Delta(\Delta_f H^\circ) = -21$ kJ/mol) in homologous series. We

Table 2
Thermochemical data for homologous aldehydes

Molecule	Δ_fH° (kJ/mol)		Recommended $\Delta_fH^\circ \pm 1.5$ (this work, kJ/mol)
	NIST[a]	Pedley[b]	
CH_3CHO	−170.7 ± 1.3	−166.1 ± 0.5	−166.5
CH_3CH_2CHO	−188.7 ± 0.8	−185.6 ± 0.9	−189
$CH_3(CH_2)_2CHO$	−211.8 ± 0.9 −204.4 ± 1.4	−204.8 ± 1.4	−207.5
$CH_3(CH_2)_3CHO$		−228.5 ± 1.7	−227
$CH_3(CH_2)_4CHO$			−248
$CH_3(CH_2)_5CHO$	−264 ± 4.2	−263.8 ± 4	−268
$CH_3(CH_2)_6CHO$	−291.9 ± 2.8		−289

[a] Ref. [2].
[b] Ref. [6].

therefore recommend that $\Delta_fH^\circ(CH_3CH_2O^\bullet) = -35 \pm 8$ kJ/mol be adopted. The above particular difficulty with the bond strengths has also been discussed by Simoes and co-workers [8].

Note that these numerical differences even apply to the free radicals $CH_3O^\bullet$, $CH_3CH_2O^\bullet$ and t-$C_4H_9O^\bullet$. For the first pair their Δ_fH° values have recently been re-appraised as 21 ± 1 and −14 ± 3 kJ/mol (viz. $\Delta\Delta_fH^\circ = -35 \pm 3$ kJ/mol) [4], while that for the tertiary radical has been revised to −86 ± 4 kJ/mol ($\Delta\Delta_fH^\circ = -72 \pm 4$ kJ/mol) [5]. Thus the free radicals display the same thermochemical behaviour, as expected on the basis of the additivity principle and including the steric effect of the bulky t-butyl group.

2.2. Homologous aldehydes

A question that deserves to be asked is whether the most recent data are necessarily the best, and therefore should always replace the earlier data given in major compilations. A case in point concerns the heat of formation of acetaldehyde, $\Delta_fH^\circ(CH_3CHO)$, that was established for many years as −166.1 ± 0.5 kJ/mol [6]. An update in the NIST [2] compilation gives $\Delta_fH^\circ = -170.7 \pm 1.5$ kJ/mol, a significant change. Is the latter a better value? The Δ_fH° data for the homologous aldehydes should obey the additivity principle, in that the incremental change in Δ_fH° per $-CH_2-$ group should be a constant, as it is for alkanes, alkanols, ethers, etc., namely 20 ± 2 kJ/mol. The available data are shown in Table 2.

Fig. 1 shows the assembled Δ_fH° data for aldehydes from Pedley et al. [6] and from NIST [2] as a function of carbon number and the line with a slope corresponding to that for the other homologous series (−20 kJ/mol/CH_2 group). The superimposed "best" line for the aldehydes is shown. The recommended Δ_fH° values for C_2 to C_8 are shown in the last column of the table.

For acetaldehyde, the recommended heat of formation supports the earlier value (−166.1 ± 0.5 kJ/mol), and is 4 kJ/mol below the most recently NIST adopted value. This small difference is not insignificant. When our revised heat of formation of acetaldehyde is combined with the C(O)–H bond dissociation energy in order to evaluate $\Delta_fH^\circ(CH_3CO^\bullet)$ the following obtains: $D(CH_3C(O)\text{–}H) = 374$ kJ/mol [7], $\Delta_fH^\circ(H^\bullet) = 218$ kJ/mol [2] and so $\Delta_fH^\circ(CH_3CO^\bullet) = -10.5$ kJ/mol, in excellent agreement with the recently re-assessed acetyl radical's Δ_fH° of −10.3 ± 1.8 kJ/mol [4].

2.3. Carbon monosulfide (CS)

The heat of formation of this simple molecule is given different values in the major data collections. That in NIST [2] is 280.33 kJ/mol (a surprisingly large number of significant figures?) and comes from a review by Chase [9]; 267 kJ/mol is from the Lias collection [10] and the CRC Handbook of Physics and Chemistry (2002) gives 240 kJ/mol, providing an unexpectedly wide range for so small a molecule. Two different approaches can be used to evaluate Δ_fH°(CS) in order to establish the best value. As in the previous example, the C–S bond dissociation energy, measured to be 713.3 ± 1.2 kJ/mol [11], combined with the atomic heats of formation, $\Delta_fH^\circ(C) = 716.68 \pm 0.45$ kJ/mol [2], $\Delta_fH^\circ(S) = 277.17 \pm 0.15$ kJ/mol [2] leads to $\Delta_fH^\circ(CS) = 280.6 \pm 1.8$ kJ/mol. Alternatively, from the ionization energy and Δ_fH° of HCS (7.499 ± 0.005 eV and 300.4 ± 8.4 kJ/mol [2]) an upper limit for $\Delta_fH^\circ(HCS^+) = 1024 \pm 8$ kJ/mol may be obtained. The proton affinity of CS has been determined as 791.5 kJ/mol [12] and $\Delta_fH^\circ(H^+) = 1530$ kJ/mol [2], hence the derived $\Delta_fH^\circ(CS) = 285.5 \pm 8$ kJ/mol is in reasonably good agreement with the current NIST value of 280.3 kJ/mol. This latter appears to be a satisfactory value.

2.4. The allylic radical $(CH_2CH)_2{}^\bullet COH$

The heat of formation of this radical has been reported to be 92.5 ± 8.4 kJ/mol [7]. This value will be assessed by considering appropriate C–H bond strengths and the effect of OH and vinyl substitution at a radical site in other related systems. If the above Δ_fH° datum is not in keeping with established trends, then a revision will be in order. The relevant data are shown in Table 3; all energies are in kJ/mol, numbers rounded to three significant figures.

The effect of vinyl substitution in the above systems (see the plain text numbers) clearly gives rise to a decrease in the bond

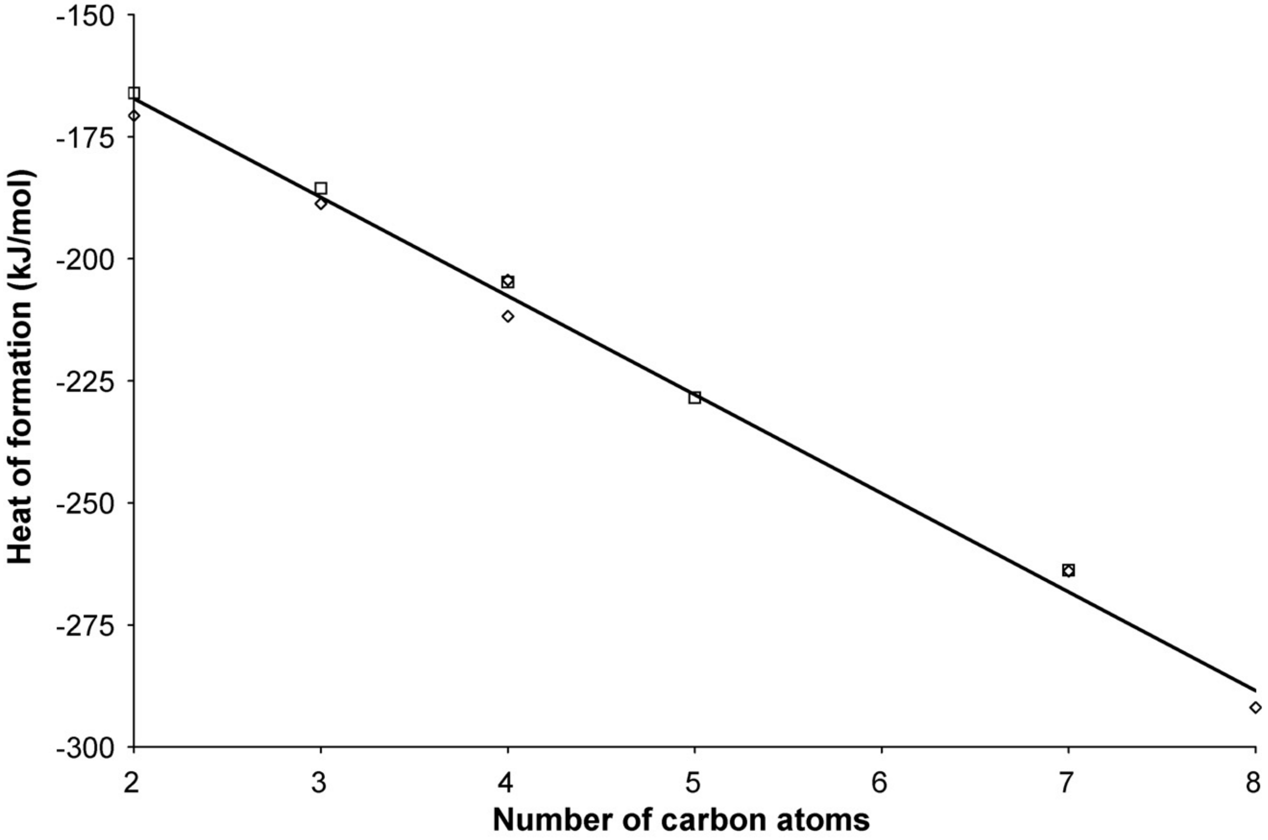

Fig. 1. Heats of formation of homologous aldehydes. The line has the slope characteristic of an *n*-alkyl series. Diamonds are from Ref. [2], squares are from Ref. [6].

dissociation energy D(C–H), resulting from the formation of a resonance stabilized radical. In methanol itself, this is observed for the first vinyl substitution, even allowing for the uncertainty in the product's $\Delta_f H^\circ$ value. For the second vinyl substitution the effect is *reversed*, even though the radical is formally resonance stabilized. This last experimental result is a clear exception and it either arises from an unidentified difficulty, such as the radical having an unusual geometry (possibly a steric effect?), or the value is simply in error.

Table 3
Bond strengths in vinyl substituted (allylic) radicals

Molecule $\Delta_f H^\circ$ in kJ/mol		D(C-H) (kJ/mol)
$CH_4 \rightarrow CH_3^\bullet + H^\bullet$		
-74[a]	147[b]	439 ± 1[b]
$CH_2{=}CHCH_3 \rightarrow CH_2CHCH_2^\bullet + H^\bullet$		
20 ± 1[a]	171 ± 3[b]	369 ± 4[b]
	176[c]	*374*[c]
$(CH_2{=}CH)_2CH_2 \rightarrow (CH_2CH)_2CH^\bullet + H^\bullet$		
106 ± 1[a]	208 ± 1[b]	320 ± 2[b]
$CH_3OH \rightarrow {}^\bullet CH_2OH + H^\bullet$		
-201[a]	-17[b]	402 ± 1[b]
$CH_2{=}CHCH_2OH \rightarrow CH_2CHCH^\bullet(OH) + H^\bullet$		
-125 ± 2[a]	0 ± 8[b]	343 ± 10
	4.5[c]	*347.5*[c]
	-22 ± 5[d]	321 ± 9[d]
$(CH_2{=}CH)_2CHOH \rightarrow (CH_2CH)_2C^\bullet(OH) + H^\bullet$		
-55[e]	93 ± 8	366 ± 9
	37[c]	*310*[c]

Using $\Delta_f H^\circ(H^\bullet) = 218$ kJ/mol [2]; [a]Ref. [6]; [b]Ref. [7]; [c]computational chemistry (see text); [d]see below for discussion; [e]by additivity [3].

Before proceeding further it is useful to check the reference data [7] for the allylic radical $CH_2CHCH^\bullet(OH)$, $\Delta_f H^\circ = 0 \pm 8$ kJ/mol. This value dates back to 1973 in a paper by Trenwith [13], who studied the pyrolysis: $CH_3CH(OH)CH{=}CH_2 \rightarrow CH_3^\bullet + CH_2CHCH^\bullet(OH)$ and determined an activation energy for this bond cleavage of 289 ± 3 kJ/mol, basing this on the temperature coefficient for the rate of formation of methane. Note however that the ancillary $\Delta_f H^\circ$ data for the methyl radical and 3-hydroxy-but-1-ene have both changed since 1973 and are now 147 and -162 ± 4 kJ/mol (by additivity [3] and using a term C–(H)(O)(C)(C_d) = −23 kJ/mol), respectively. Note that for the latter the same result obtains from estimating the effect of methyl substitution at C1 in allyl alcohol, $\Delta_f H^\circ(CH_2{=}CHCH_2OH) = -124 \pm 2$ kJ/mol by adding the $\Delta\Delta_f H^\circ$ for going from a primary to a secondary alkanol, namely -38 ± 0.5 kJ/mol. The resulting $\Delta_f H^\circ(CH_2CHCH^\bullet(OH))$ using the Trenwith data is now -22 ± 7 kJ/mol and so the corresponding bond strength, D(C–H) becomes 321 ± 9 kJ/mol. This is a surprisingly large, and therefore suspect, stabilization energy.

3. Computational chemistry

To address this and the problem of the di-vinyl substituted ${}^\bullet CH_2OH$ radical, the heats of formation of the

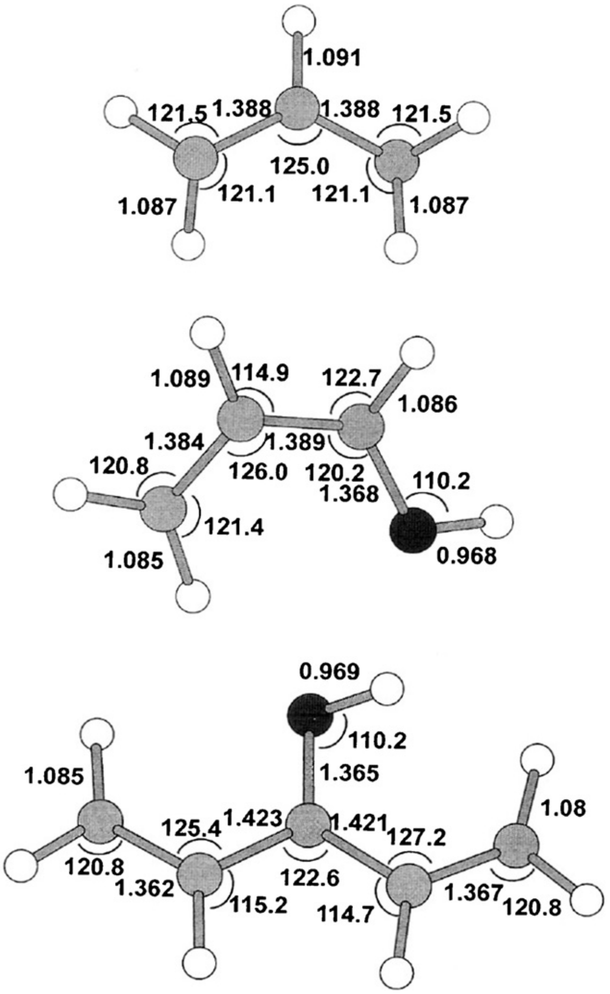

Fig. 2. The computed geometries of the radicals $^\bullet CH_2CHCH_2$, $CH_2CHCH^\bullet(OH)$ and $(CH_2CH)_2C^\bullet(OH)$. See text for details and discussion.

allyl, 1-hydroxyl-allyl and 3-hydroxy-3-pent-1,4-dienyl radicals were calculated by us at the G3 level of theory [14], using their B3LYP derived geometries [15]. The results were: $\Delta_f H^\circ(CH_2CHCH_2^\bullet) = 176$ kJ/mol, in excellent agreement with experiment, $\Delta_f H^\circ(CH_2CHCH^\bullet(OH)) = 4.5$ kJ/mol and $\Delta_f H^\circ((CH_2CH)_2C^\bullet(OH)) = 37$ kJ/mol, leading to the bond strengths shown in the above table. Note that the optimised geometries of these three allylic radicals, shown in Fig. 2, were essentially the same, with no distortion of the coplanar carbon skeleton. For the radical $CH_2CHCH^\bullet(OH)$, $\Delta_f H^\circ = 4.5$ kJ/mol is in good agreement with the original experimental result. We argued that the ancillary data used in that work were flawed and the revised data gives $\Delta_f H^\circ(CH_2CHCH^\bullet(OH)) = -22.5 \pm 5$ kJ/mol, in bad agreement with the computed value. We suggest therefore that the activation energy from the pyrolysis may be too low by some 20 kJ/mol. We also propose that the reference value for $\Delta_f H^\circ((CH_2CH)_2C^\bullet(OH)) = 93$ kJ/mol [7] is seriously flawed and that the newly calculated value of 37 kJ/mol should be adopted.

Note too, that the effect of –OH substitution in the above hydrocarbon radicals is almost constant at -167 ± 3 kJ/mol and that vinyl substitutions in $CH_3^\bullet$ and in $^\bullet CH_2OH$ behave in a similar fashion. This would be expected on the basis of additivity considerations.

4. Summary

The message that we would like to send from this short paper is that thermochemical data should always be viewed with a critical eye. This can be achieved by considering the datum of interest in relation with those for similar molecular species, by considering its consequences for, e.g., a bond dissociation energy, for the heat of formation of a related free radical, odd or even electron ion, etc. We have indicated by example how this can work in practice. If a wholly new value for a neutral is required, it may confidently be assessed by the proper use of the additivity principle or a simple extension thereof. Of course, the difficulty may also satisfactorily be resolved by the use of computational chemistry, but the problem itself must first have been identified by the above inspection procedures.

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