A new procedure for estimating the enthalpies of formation for $RCH_2^{\cdot}$ free radicals

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DOI: 10.1070/MC2000v010n01ABEH001122

From the observed regularity that for certain substituents the $\Delta\Delta H_f^0$ values for $Me^{\cdot} \rightarrow RCH_2^{\cdot}$ free radicals and $CH_2{=}CH_2 \rightarrow RCH{=}CH_2$ molecules are nearly identical, new or corrected values for the enthalpies of formation were estimated for about 30 gaseous free radicals and molecules.

It is known that the H → Me replacement in hydrocarbon molecules gives different $\Delta\Delta H_f^0$ (ΔH_f^0 shift) values: *ca.* –20.9 kJ mol^{-1} in alkanes, –33.5 for $CH_2{=}CH_2 \rightarrow MeCH{=}CH_2$ or –43.3 kJ mol^{-1} for $HC{\equiv}CH \rightarrow MeC{\equiv}CH$ replacement.[1,2] The observed tendencies could be explained by the increasing electronegativity (EN) value of the carbon atom in $sp^3 \rightarrow sp^2 \rightarrow sp$ hybridization accompanied by a stabilization effect of the Me group. We observed that for certain substituents the $\Delta\Delta H_f^0$ values for $Me^{\cdot} \rightarrow RCH_2^{\cdot}$ free radicals and $CH_2{=}CH_2 \rightarrow RCH{=}CH_2$ molecules are very close with minor deviations < 6.5 kJ mol^{-1} which is in the range of mean accuracy of $\Delta H_f^0(R^{\cdot})$ determination (Table 1). This fact can be indicative of nearly identical charges at C-atoms of both the $Me^{\cdot}$ free radical and the ethylene molecule or of their nearly identical EN values.

Let us comment data presented in Table 1. The experimental ΔH_f^0 ($ClCH{=}CH_2$) = 37.2 kJ mol^{-1} was criticised,[5,6] and the new value 21.7 kJ mol^{-1} (ref. 5) was computed [the brief form of ΔH_f^0 instead of the full form of ΔH_f^0 (gas; 298.15 K) is used in the text]. An analysis of the thermochemistry of ROH and their fluorinated analogues RF[2,9] displayed the $\Delta\Delta H_f^0$ (ROH → RF) of *ca.* –(20–25) kJ mol^{-1} and thus ΔH_f^0 ($FCH_2CH{=}CH_2$) = = –148.5 was taken from ΔH_f^0 = –122.0 kJ mol^{-1} (ref. 1) for $HOCH_2{-}CH{=}CH_2$ instead of the estimated values –155 (ref. 7) or –172 kJ mol^{-1} (ref. 8). For checking the known and finding the new values of the enthalpies of formation for free radicals we widely used isodesmic reactions[2,3,6,9] originally suggested by Benson.[12] For example:

$$\begin{array}{lccccccccc} & {}^{\cdot}CH_2OH & + & MeF & \longrightarrow & MeOH & + & {}^{\cdot}CH_2F & + & Q \\ \Delta H_f^0/\mathrm{kJ\ mol^{-1}}: & -17.6^{3} & & -228.0^{2,9} & & -201.5^{1} & & -32.0^{3,13} & & -12.1 \end{array} \qquad (1)$$

An isodesmic ‘reaction’ is a hypothetical reaction, but like any reaction, its enthalpy is related to the enthalpies of formation of reactants and products. We define Q as $-\Delta H_{\mathrm{reaction}}$ for convenience; $-Q$ measures the deviation from bond additivity. If $Q > 0$, the free radical in the right-hand side of an isodesmic reaction is more stable than that in the left-hand side, and at $Q < 0$ the free radical in the right-hand side (${}^{\cdot}CH_2F$) is less stable than the free radical (${}^{\cdot}CH_2OH$) in the left-hand side of equation (1). Equations (2) demonstrate the most important regularity in the stabilities of free radicals: a less stable free radical extracts a larger stabilising effect from the same substituent (here Me) than a more stable one (ΔH_f^0 and Q values in kJ mol^{-1}):

$$\begin{tikzcd} \begin{array}{c}{}^{\cdot}SH\\ 144.3^{2,3}\end{array} \arrow[r, "-56.1"] \arrow[d, "+12.5"] & \begin{array}{c}Me^{\cdot}\\ 145.6^{2,3}\end{array} \arrow[r, "-18.0"] \arrow[d, "+25.1"] & \begin{array}{c}{}^{\cdot}NH_2\\ 192.5^{2,3}\end{array} \arrow[r, "-48.7"] \arrow[d, "+39.7"] & \begin{array}{c}{}^{\cdot}OH\\ 39.3^{2,3}\end{array} \arrow[d, "+62.3"] \\ \begin{array}{c}MeS^{\cdot}\\ 129.7^{2,3}\end{array} & \begin{array}{c}MeCH_2^{\cdot}\\ 110.9^{2,3}\end{array} & \begin{array}{c}MeNH^{\cdot}\\ 177.4^{2,3}\end{array} & \begin{array}{c}MeO^{\cdot}\\ 17.6^{2,3}\end{array} \end{tikzcd} \qquad (2)$$

The isodesmic reactions in (2) are given in the brief form ${}^{\cdot}SH \rightarrow MeS^{\cdot}$ instead of the full form ${}^{\cdot}SH + MeSH \rightarrow H_2S + MeS^{\cdot} + Q$ because the structures of the molecules taking part in isodesmic reactions are obvious.

We represent the application of isodesmic reactions to deduce the correct value of ΔH_f^0 for ${}^{\cdot}CH_2SH$. If we involve a currently used value of 151.9 kJ mol^{-1} (refs. 10, 13) in isodesmic reactions (3), we see the inconsistency of Q values with thermochemical properties of free radicals: ${}^{\cdot}CH_2OH$ free radical being slightly more stable than ${}^{\cdot}CH_2F$ ($Q < 0$ for ${}^{\cdot}CH_2OH \rightarrow {}^{\cdot}CH_2F$) should give the Q' value more negative than Q'' [compare with equation (2)] but not a positive one (the ΔH_f^0 values were taken from refs. 1 and 2):

$$\begin{tikzcd} \begin{array}{c}{}^{\cdot}CH_2OH\\ -17.6^{3,13}\end{array} \arrow[r, "-12.1", "Q"'] \arrow[d, "Q'"', "+8.9"] & \begin{array}{c}{}^{\cdot}CH_2F\\ -31.8^{3,13}\end{array} \arrow[d, "Q''"', "-9.6"] \\ \begin{array}{c}{}^{\cdot}CH_2SH\\ 151.9^{10,13}\end{array} & \begin{array}{c}{}^{\cdot}CH_2Cl\\ 121.3^{3,13}\end{array} \end{tikzcd} \qquad (3)$$

$$\begin{tikzcd} \begin{array}{c}{}^{\cdot}CH_2NH_2\\ 149.4^{2,10}\end{array} \arrow[r, "-11.3"] \arrow[d, "{[-21]}"] & \begin{array}{c}{}^{\cdot}CH_2OH\\ 17.6\end{array} \arrow[r, "-12.1"] \arrow[d, "-14.6"] & \begin{array}{c}{}^{\cdot}CH_2F\\ -31.8\end{array} \arrow[d, "-9.6"] \\ \begin{array}{c}{}^{\cdot}CH_2PH_2\\ {[194.6]}\end{array} & \begin{array}{c}{}^{\cdot}CH_2SH\\ 175.7^{2,3}\end{array} & \begin{array}{c}{}^{\cdot}CH_2Cl\\ 121.3^{3,13}\end{array} \end{tikzcd} \qquad (4)$$

In general, the electron-donor properties (which stabilise free radicals centres) of the substituents comprising the elements of the third row of the Periodic Table are smaller than those for the elements of the second row: Cl < F, S < O and P < N. For example, the σ_p^+ and R (resonance) constants are more positive (destabilization) for the elements of the third row.[14] Therefore, the ΔH_f^0 value 175.7 kJ mol^{-1} for ${}^{\cdot}CH_2SH$ fits better the above properties of the elements (equations 4). We also obtain $Q \sim -20$ kJ mol^{-1} by extrapolation for the ${}^{\cdot}CH_2NH_2 \rightarrow {}^{\cdot}CH_2PH_2$ isodesmic reaction and taking $\Delta H_f^0({}^{\cdot}CH_2PH_2)$ = –20.9 kJ mol^{-1} (ref. 2) we obtain ΔH_f^0 (${}^{\cdot}CH_2PH_2$) = 194.6 kJ mol^{-1}. Next, calculating $\Delta\Delta H_f^0$ ($Me^{\cdot} \rightarrow {}^{\cdot}CH_2PH_2$) = 49.0 kJ mol^{-1}, we get the previously unknown value of $\Delta H_f^0(CH_2{=}CHPH_2) = \Delta H_f^0(CH_2{=}CH_2)$ (52.5) + + 48.9 = 101.4 kJ mol^{-1}.

The enthalpies of formation for some of the free radicals collected in Table 1 or discussed in the text were also estimated using the group additivity with non-linear correction (GANLC) method.[15–18] The method was successfully used for verifying, correcting or getting new values for about 350 free radicals and carbene-like species from diverse classes of hydrocarbons and heteroatomic compounds.[19] The GANLC method is represented by three versions in which three different levels of approximation are used. The method is based on the introduction of the variable group contribution to free radical thermochemistry as compared with earlier suggested constant group contributions.[12] For example, in the $XC^4H_2C^3H_2C^2H_2C^1H_2^{\cdot}$ free radical the group contributions of $-CH_2-$ (2), $-CH_2-$ (3) or $-CH_2-$ (4) differ from those in neutral molecules reflecting the effect of the free radical centre on the thermochemical properties of these groups. The GANLC method was detailed in refs. 15–18. The reliability of the method is further confirmed in this work. Thus, the value 177.4 kJ mol^{-1} was obtained for the ${}^{\cdot}CH_2SH$ free radical supporting the suggested value 175.7 kJ mol^{-1} (Table 1). For the $ClCH_2CH_2^{\cdot}$ and $HOCH_2CH_2^{\cdot}$ free radicals, the values 92.9 and

Table 1 $\Delta\Delta H_f^0$(g) values for Me$^\bullet$ → RCH$_2^\bullet$ free radicals and CH$_2$=CH$_2$ → RCH=CH$_2$ molecules (ΔH_f^0 and $\Delta\Delta H_f^0$ in kJ mol^{-1}).

RCH$_2^\bullet$	ΔH_f^0(RCH$_2^\bullet$)	$\Delta\Delta H_f^0$(A) Me$^\bullet$ → RCH$_2$	RCH=CH$_2$	ΔH_f^0(RCH=CH$_2$)	$\Delta\Delta H_f^0$(B) C$_2$H$_4$ → RCH=CH$_2$	Δ A → B
Me$^\bullet$	145.6[1]		CH$_2$=CH$_2$	52.5[1]		
MeCH$_2^\bullet$	110.9[2,3]	–34.7	MeCH=CH$_2$	20.0[1]	–32.5	+2.2
HOCH$_2$CH$_2^\bullet$	–29.3[2]	–174.9	HOCH$_2$CH=CH$_2$	–124.5[1]	–177.0	–2.1
	–31.0[3,4]	–176.6				–0.4
ClCH$_2^\bullet$	121.3[2,3]	–24.3	ClCH=CH$_2$	21.8[5,6]	–30.7	+6.4
FCH$_2$CH$_2^\bullet$	–56.5[3]	–202.1	FCH$_2$CH=CH$_2$	–172.0[8]	–224.5	–22.4
				–154.8[7]	–207.3	–5.2
				[–148.5][9]	–201	+1.1
BrCH$_2^\bullet$	169.4[3]	+23.8	BrCH=CH$_2$	79.2[1]	+26.7	+2.9
				[75.4]	+22.9	–0.9
ICH$_2^\bullet$	228.0[3]	+82.4	ICH=CH$_2$	134.7[2,7]	+82.2	–0.2
H$_2$NCH$_2^\bullet$	149.4[3]	+3.8	H$_2$NCH=CH$_2$	[57.0][2,7]	+4.5	+0.7
HSCH$_2^\bullet$	151.9[10]	+6.3	HSCH=CH$_2$	[82.4]	+29.9	+23.6
	175.7[2,3]	+30.1				–0.2
ClCH$_2$CH$_2^\bullet$	91.2[11]	–54.4	ClCH$_2$CH=CH$_2$	[1.2]	–51.3	+3.1
Me$_2$CH$^\bullet$	77.8[2,3]	–67.8	Me$_2$C=CH$_2$	–16.9[1]	–69.4	–1.6
MeCHCl$^\bullet$	72.0[10]	–73.6	MeC(Cl)=CH$_2$	–20.9[1]	–73.4	+0.2
Cyclobutyl radical	214.6[10]	+69.0	Methylidenecyclobutane	121.3[1]	+68.8	–0.2
Cyclopentyl radical	105.0[10]	–40.6	Methylidenecyclopentane	12.1[1]	–40.4	–0.2

–33.9 kJ mol^{-1}, respectively, were calculated, which are very close to the data in Table 1. The value of ΔH_f^0 estimated by the GANLC method for 3-cyanocyclobutyl free radicals is 338.9 or 343.0 kJ mol^{-1} which was derived from either 251 or 255 kJ mol^{-1}, respectively, for NCCH$_2$CH$_2^\bullet$ free radicals.

We used the regularities represented in Table 1 for either getting new values of the enthalpies of formation for RCH$_2^\bullet$ free radicals from the known or estimated values of the enthalpies of formation for RCH=CH$_2$ molecules or *vise versa*. For estimation of ΔH_f^0(RCH=CH$_2$), we used the earlier found observation[2,7,9] that $\Delta\Delta H_f^0$(RPh → RCH=CH$_2$) replacement gives the more or less permanent value –30 kJ mol^{-1}. Since the ΔH_f^0 values for RPh molecules are widely represented in the literature,[1] those for ΔH_f^0(RCH=CH$_2$) can be reliably estimated. For example, taking ΔH_f^0 values for PhNH$_2$, PhSH and PhBr to be 87.0, 112.4 and 105.4[1] kJ mol^{-1}, respectively, and $\Delta\Delta H_f^0$(RPh → RCH=CH$_2$) –30 kJ mol^{-1}, we get 57.0, 82.4 and 75.4 kJ mol^{-1} for the enthalpies of formation for CH$_2$=CHNH$_2$, CH$_2$=CHSH and CH$_2$==CHBr molecules, respectively.

Using the found regularity that the $\Delta\Delta H_f^0$ values for radicals and molecules are identical and the known data on ΔH_f^0 of RCH=CH$_2$ molecules, either experimental[1] or estimated from known data on RPh,[1] EH$_4$, EMe$_4$ and EPh$_4$ molecules[20–24] (E = = Si, Ge, Sn, Pb) and $\Delta\Delta H_f^0$ (RCH=CH$_2$ → RPh) ~ 30 kJ mol^{-1} (refs. 2, 7 and 22), the following new values for the enthalpies of formation for free radicals were obtained (kJ mol^{-1}): CH$_2$==CHCH$_2$CH$_2^\bullet$ 198.7; PhCH$_2$CH$_2^\bullet$ 228.0; 2-bicyclo[2,2,2]octyl radical 83.7; BrCH$_2$CH$_2^\bullet$ 138.1; ICH$_2$CH$_2^\bullet$ 190.4; CH$_2$=CHOCH$_2^\bullet$ 79.5; $^\bullet$CH$_2$OAc –221.7; $^\bullet$CH$_2$CH$_2$C(O)OEt –261.5; $^\bullet$CH$_2$OC(O)Ph –98.3; $^\bullet$CH$_2$OPh 115.1; H$_2$NNHCH$_2^\bullet$ 265.7; NCCH$_2$CH$_2^\bullet$ 255.2; 3-cyanocyclobutyl radical 347.3; HSCH$_2$CH$_2^\bullet$ 154.8; EtS(O)–CH$_2$CH$_2^\bullet$ –10.5; *p*-MeC$_6$H$_4$SO$_2$CH$_2$CH$_2^\bullet$ 108.8; $^\bullet$CH$_2$PH$_2$ 194.6; $^\bullet$CH$_2$At 284.5; H$_3$ECH$_2^\bullet$ 165.3, 240.6, 324.3, 405.8 (E = Si, Ge, Sn or Pb, respectively).

A new estimation procedure for the enthalpies of formation of RCH$_2^\bullet$ free radicals can be applied to RR′CH$^\bullet$ (Table 1) and other organoelement free radicals.

This work was supported by INTAS (grant no. 96-1990).

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Received: 25th February 1999; Com. 99/1450