Internet Electronic Conference of Molecular Design **2003**, November 23 – December 6
BioChem Press http://www.biochempress.com

Prediction of R-H Homolytic Bond Dissociation Energies from Gas-Phase IR Data on ν_{CH} Values

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Abstract

The main goal of this work is the application of ν_{CH} IR frequencies of gaseous R-H molecules to thermochemistry of carbon-centered R• free radicals. For the first time the variable $\Delta\nu_{CH}$ (in R-H molecules) per 1 kcal mol^{-1} in bond dissociation energies are suggested: 9 cm^{-1} for alkanes, 11 cm^{-1} for C-H bond in alkenes, 12 cm^{-1} in RC≡C-H and 14 cm^{-1} for RC$\underline{H}$=O molecules. This being accepted the exact ΔH_f^0 values for several key aliphatic free radicals (Me_3C•, •CH_2OH, •CH_2NH_2, •CH_2NHMe, •CH_2NMe_2) and the novel values for 12 substituted ethynyl RC≡C• radicals are suggested. For the latter, the specific role of polarizability of substituent R in stabilization of radical center is demonstrated.

The limitations and difficulties in application of IR spectra to free radicals' thermochemistry are analyzed. The absence of low lying ("adiabatic") C-H bond in many CH_3X molecules and the observation of these bonds at much (by 60-180 cm^{-1}) higher frequencies compared with expected ones makes questionable the application of IR spectra to these purposes. However, the small deviations by 20-40 cm^{-1} can be well treated by isodesmic reactions control and Raman spectra for prediction of "lost" frequency and ΔH_f^0 of free radical as it was demonstrated for •CH_2OCH_3 and Me_3CCH_2• radicals.

Keywords. Thermochemistry, free radicals, IR spectroscopy, isodesmic reactions

Despite the obvious importance of knowledge of accurate values of the enthalpies of formation of free radicals for synthesis, chemical kinetics, chemistry of atmosphere and combustion, biochemistry, spectroscopy considerable uncertainty about these values remains. The range of known values for many of them is large and no tendency is observed to make this range more narrow. For example, this range for vinyl C_2H_3• free radical encompasses 63.0-75.7, for ethynyl HC≡C• 110.4-139, for cyanoethynyl N≡CC≡C• 132-178.2, for •COOH –44.7-(-62.6), C_6F_5• -89.7-(-143.2), Me_3Si• -25.1-(+14.9), PH_2• 22-39, for AlH_2• 40-71 kcal mol^{-1} (see Refs 1-5 and references therein). Even for Et•, Me_2CH•, Me_3C•, Me_3CCH_2• alkyl free radicals there is no common opinion about their enthalpies of formation (see Ref.2).

Recently [1-5 and Refs therein) the general procedure of the series of isodesmic reactions has been elaborated for checking the known values and correcting or finding novel values of the enthalpies of formation for free radicals. Here, we further present the application of this methodology to thermochemistry of free radicals this time for analysis of gas phase $\nu_{C\underline{H}}$ isolated frequencies in gas phase IR spectra of R-H molecules and its correlation with the relative

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thermodynamic stabilities of R• free radicals. The correlation of stretching frequencies with chemical and physical properties is a popular and sometimes instructive occupation. In many works the correlations between isolated $\nu_{C\underline{H}}$ frequencies (in $RC\underline{H}D_2$, $RC\underline{H}DR'$ and $R(R')(R'')C\underline{H}$ molecules with C-H bond dissociation energies (BDEs) have been performed (see Refs 6-13 and references therein). For a number of reasons a reexamination of these correlations is now timely.

Positive results. Earlier, to derive the BDE values from $\nu_{C\underline{H}}$ data the unique ratio 11 cm^{-1} in $\Delta\nu$ equivalent to 1 kcal mol^{-1} of ΔBDE was applied for *all* types of C-H bonds [6]. In present work we propose for the first time (see also Refs 1 and 5) the *variable* values for this interrelationship which depend on electronegativity (EN) of C-atom.

To find out the $\Delta\nu$ value corresponding to 1 kcal mol^{-1} in ΔBDE for aliphatic C-H bond we take two key examples (Eqns 1 and 2).

$$C\underline{H}_4 \xrightarrow[Q_1 = [10.97]]{\Delta\nu = -98.7 cm^{-1}} Me_3C\underline{H} \qquad (1)$$

$\nu_{C\underline{H}}$ 2992 [10] 2893.3 [10]

$\Delta\nu$/1 kcal mol^{-1}	Q_1 (kcal mol^{-1})	$\Delta H_f^0(Me_3C\bullet)$ (kcal mol^{-1})
14 cm^{-1}	7.05	13.76
12	8.22	12.59
11	8.97	11.84
10	9.87	10.94
9	10.97	9.84
8	12.34	8.47
6	16.45	4.36

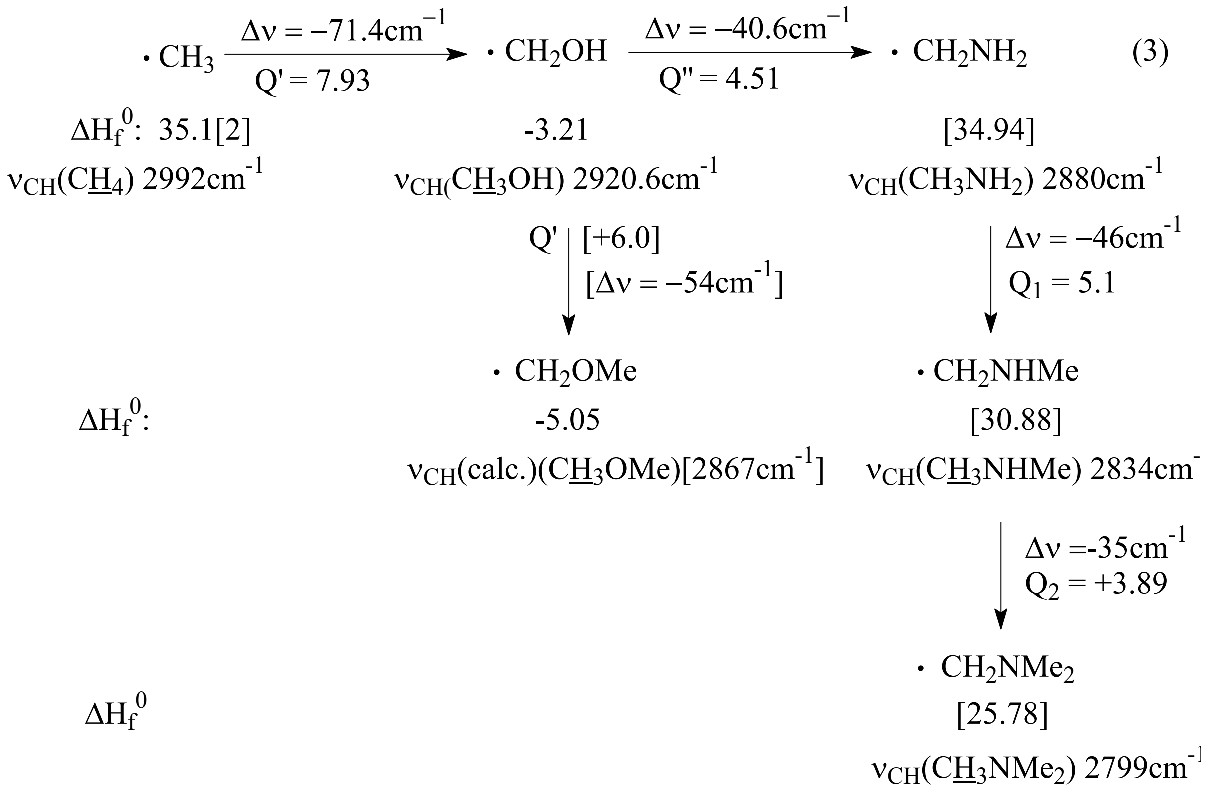
$$C\underline{H}_4 \xrightarrow[Q_2 = [7.93]]{\Delta\nu = -71.4 cm^{-1}} C\underline{H}_3OH \qquad (2)$$

$\nu_{C\underline{H}}$ 2992 [10] 2893.3 [10]

$\Delta\nu$/1 kcal mol^{-1}	Q_2 (kcal mol^{-1})	$\Delta H_f^0(\bullet CH_2OH)$ (kcal mol^{-1})
11cm^{-1}	6.49	-1.77
10	7.14	-2.42
9	7.93	-3.21
8	8.93	-4.21
7	10.20	-5.48

In both equations we take a set of diverse random $\Delta\nu$ values corresponding to 1 kcal mol^{-1} in ΔBDE. Then dividing the experimental $\Delta\nu$ (-98.7 cm^{-1}) by each of these values we obtain diverse Q_1 (or Q_2) values and then applying the full form of isodesmic reaction we gain diverse ΔH_f^0 values of $Me_3C\bullet$ (Eqn 1) or $\bullet CH_2OH$ (Eqn 2) radicals. For ΔH_f^0 $Me_3C\bullet$ radical the range of quoted values is 4.5-14.3 kcal mol-1 (Ref.2 and references therein). Computation gives higher values compared with experimental ones, e.g. 13.5 [14] or 14.3 [15] kcal mol^{-1}. In Ref.2 the detailed analysis of the thermochemistry of alkyl radicals was performed using series of isodesmic reactions and finally the ΔH_f^0 value ~ 9.9 kcal mol-1 for $Me_3C\bullet$ radical was insistently advocated. This value corresponds to $\Delta\nu$ 9 cm^{-1}/1 kcal mol^{-1} (Eqn 1) being also close to the mean value of the quoted values. Q_1 value is the heat of isodesmic reaction $CH_3\bullet + Me_3CH \rightarrow CH_4 + Me_3C\bullet + Q_1$ (full form) or $CH_3\bullet \rightarrow Me_3C\bullet + Q_1$ (Eqn 1, brief form). For $\bullet CH_2OH$ radical the following values gained from chemical kinetics and photoionization studies are known: -6.2 [16], -5.1 [17], -4.08 [18], -3.5 [19], -2.9 [20], -2.5 [19], -2.15 [21] kcal mol^{-1}. Thus, we see that $\Delta\nu$ (9 cm^{-1}) leads to ΔH_f^0 $Me_3C\bullet$ and $\bullet CH_2OH$ 9.84 and –3.21 kcal mol^{-1}, respectively, which are self-consistent and are close to the mean values quoted in the literature.

Now we come to Eqn 3 (ν_{CH} values – from Refs 6, 10, 12; ΔH_f^0 and Q values – in kcal mol^{-1}, the derived values – in square brackets; the isodesmic reactions are given in brief forms, e.g.$\bullet CH_3 \rightarrow \bullet CH_2OH + Q$ instead of .$\bullet CH_3 + CH_3OH \rightarrow CH_4 + \bullet CH_2OH + Q$; the ΔH_f^0 values for molecules used in isodesmic reactions are taken from Ref. 22):



(3)

Q values originate from full forms of isodesmic reactions, e.g. from brief form of .$\bullet CH_3 \rightarrow \bullet CH_2OH + Q'$ isodesmic reaction we have $Q = \Delta H_f^0(CH_3\bullet) + \Delta H_f^0(CH_3OH) - \Delta H_f^0(\bullet CH_2OH) - \Delta H_f^0(CH_4) = 35.1 - 48.16 - (-3.21) - (-17.78) = 7.93$ kcal mol^{-1} (Eqn 3).

Since $\bullet CH_2OH$ radical is by ~ 4.5 kcal mol^{-1} (Q'') *less* stable than $\bullet CH_2NH_2$ free radical it is expected that in $\bullet CH_2OH \rightarrow \bullet CH_2OMe$ isodesmic reaction $Q' > Q_1$ since the less stable $\bullet CH_2OH$ radical might extract higher stabilization effect from the same (here, Me) group (see Refs 2-4 and compare Q_2 and Q_1 values in Eqn 3). Taking an arbitrary Q' value ~ 6 kcal mol^{-1} (Q' and Q_1 would not differ much since Q'' value, i.e. difference in thermodynamic stabilities of $\bullet CH_2OH$ and

•CH_2NH_2 radicals is also not large) we get ΔH_f^0 (•CH_2OMe) = ΔH_f^0 (•CH_2OH) - ΔH_f^0 (CH_3OH) + ΔH_f^0 (CH_3OCH_3) – Q' = -3.21 – (-48.16) – 44.0 – 6.0 = -5.05 kcal mol^{-1} and ν_{CH} ($C\underline{H}_3OMe$) = ν_{CH} ($C\underline{H}_3OH$) – Q' x 9 cm^{-1} = 2920.6 – 6 x 9 = 2866.6 cm^{-1}. This band is not fixed in IR spectrum but rather at 2883.4 cm^{-1} [6]. This being applied in Eqn 3 gives Q' 4.18 kcal mol^{-1} which does not fit the accurate and self-consistent data on ν_{CH} values for methylated amines. In Raman spectrum of gaseous CH_3OCH_3 molecule there is a band at 2868 cm^{-1} [23] which might correspond to IR ν_{CH} (calc.) 2866.6 cm^{-1}. Another candidate for the low lying band comes from IR spectrum of liquid CH_3OCH_3 molecule exhibiting strong band at 2845 cm^{-1} [24]. The corresponding band for gaseous molecule is expected to occur at slightly higher frequency 2850-2855 cm^{-1} (when solvent effect is taken in consideration) and hence ΔH_f^0 (CH_3OCH_2•) radical will be about –6.5 kcal mol^{-1}. This gives O' ~7.5 kcal mol^{-1} which, in general, fits the data of Eqn 3. The experimental data for ΔH_f^0 (CH_3OCH_2•) are –2.8±1.2 [16], -5.0 [25] or –6.9 [26] kcal mol^{-1}.

The ΔH_f^0 values of aminomethyl radicals (Eqn 3) 34.9, 30.9 and 25.8 gained from IR spectra although are close to literature values [Ref. 16] 35.7±2, 30.1±2 and 26.1±2 kcal mol^{-1} for •CH_2NH_2, •CH_2NHMe and •CH_2NMe_2 radicals, respectively (thus once more supporting the reliability of our $\Delta\nu$ 9 cm^{-1} per 1 kcal in ΔBDE), but are more accurate and self-consistent. Earlier, it was found [2] that for both ions (cations and radical-cations) and free radicals the consecutive H → Me substitution gave Q_2/Q_1 0.55±0.05 when this takes place at α-position to unsaturated carbon and Q_2/Q_1 ~ 0.75±0.05 when H → Me replacement occurs in β-position to cationic or radical-cationic centers. From Eqn 3 we gain Q_2/Q_1 0.75 for aminomethyl radicals whereas Q_2/Q_1 is 0.42 if we use the data gained from kinetics [16].

Taking the accurate values for ΔH_f^0 HC(•)=O 10.1 [27] and •$COOCH_3$ –40.4 [16] kcal mol^{-1} and $\Delta\nu$ ($C\underline{H}_2=O$ → $\underline{H}COOMe$ = 117 cm^{-1} [6] we obtain Q – 9.47 kcal mol^{-1} for HC(•)=O + $HCOOCH_3$ → $H_2C=O$ + •COOMe + Q isodesmic reactions and 117 : 8.47 = 13.81 ~ 14 cm^{-1} for 1 kcal mol^{-1}. From this and the value 9 cm^{-1} for C-H bond in substituted alkanes (see above) it is clear that $\Delta\nu_{CH}$/1 kcal mol^{-1} value depends on the electronegativity (EN) of C-atom. There are no accurate experimental data for even two $CH_2=C$(•)H and $CH_2=C$(•)R (or RCH=CH•) or HC≡C• and any RC≡C• free radicals. Therefore, we, taking $\Delta\nu_{CH}$/BDE 9 cm^{-1} for alkanes, 14 cm^{-1} for $R\underline{C}H=O$ molecules and EN values 4.5-4.8; 5.3, 5.8 and 7.4 units for alkyl, $CH_2=CH$, HC≡C and CHO groups (from Ref.1) we assign approximately $\Delta\nu_{CH}$ 11 and 12 cm^{-1} equivalent to 1 kcal mol^{-1} in ΔBDE (C-H) in alkenes and acetylenes, respectively. This finding allows to apply the data on gas phase IR spectra for description of the free radicals' heats of formation more accurately than it was done before when a unique value ~ 11 cm^{-1} was used for any type of C-H bond.

Now we come to calculation of the heats of formation for substituted ethynyl RC≡C• free radicals from IR spectra of RC≡C-H molecules. But to perform this we have to select the correct ΔH_f^0 value for unsubstituted ethynyl HC≡C• radical for which the experimental values (originating from pyrolysis and bimolecular chemical kinetics, diverse spectroscopic methods, ionization and appearance potential measurements) range from 110 to 139 kcal mol^{-1} while enumerous ab initio and semi-empirical methods (including wide variation of model systems) give hundreds of values ranging from 87 to 163 kcal mol^{-1} (for details see Ref.1). Our computation results using PM3, AM1, MNDO, three ab initio methods and 21 isodesmic reactions gave 126 values in the range 50.6-177.3 kcal mol^{-1}. A disappointing result! The photofragmentation of acetylene molecule appeared to be a very complex process depending on method of investigation. From analysis of 17 experimental works on spectroscopy, photodissociation, photoionization, pyrolysis of acetylene we arrived to the decision to ascribe ΔH_f^0 $HC\equiv C\bullet$ 123±2 kcal mol^{-1} (Ref.1). The details of the arguments in favor of this value are given in Ref.1. Here we give a single one. Let us consider the isodesmic reaction (Eqn 4)(ΔH_f^0 and Q – in kcal mol^{-1})

	$\cdot C\equiv N$ +	$HC\equiv CH$ $\longrightarrow$	$HC\equiv N$ +	$HC\equiv C\cdot$ +	Q	(4)
ΔH_f^0	104	54.5	32.6	135 [28]	-9.1	
				131 [29, 30]	-5.1	
				[125.9]	0	
				123* ±2	+2.9*	
				122 [31]	+3.9	
				120.5 [32]	+5.4	

*) this work

ΔH_f^0 $\bullet C\equiv N$ 104.1±0.5 was determined experimentally by three methods [33].The higher value is quoted 105.5 kcal mol^{-1} [34]. Tsang "insisted" on much lower value 99 kcal mol^{-1} [35]. There is also a novel experimental value [36] for HCN molecule 30.8 kcal mol^{-1}. From the well documented properties of $HC\equiv C$- and $N\equiv C$- groups [1, 22, 28, 31, 37, 38] the latter is a stronger electron-withdrawing group than the former thus making Q > 0 in Eqn 4. Since it is not possible to evaluate the Q value in Eqn 4, for a moment we accept the value 123 kcal mol^{-1} for ΔH_f^0 $HC\equiv C\bullet$ radical as the most reliable. If ΔH_f^0 $\bullet C\equiv N$ 99 kcal mol^{-1} [35] is accepted then ΔH_f^0 $HC\equiv C\bullet$ will further go down.

The experimental data on ΔH_f^0 values of substituted ethynyl $RC\equiv C\bullet$ radicals are not available whereas there is a wealth of ν ($RC\equiv C$-H) values in gas phase IR spectra. Using these data (for literature sources see Ref.1), the ΔH_f^0 values for parent molecules $RC\equiv CH$ which are also calculated in Ref.1 using enthalpic shift procedure and $\Delta\nu_{CH}/\Delta BDE$ 12 cm^{-1} equivalent for 1 kcal mol^{-1} we calculated the heats of formation for many $RC\equiv C\bullet$ free radicals (SE – stabilization energy, ΔH_f^0 values in kcal mol^{-1}, all literature sources are given in Ref.1)

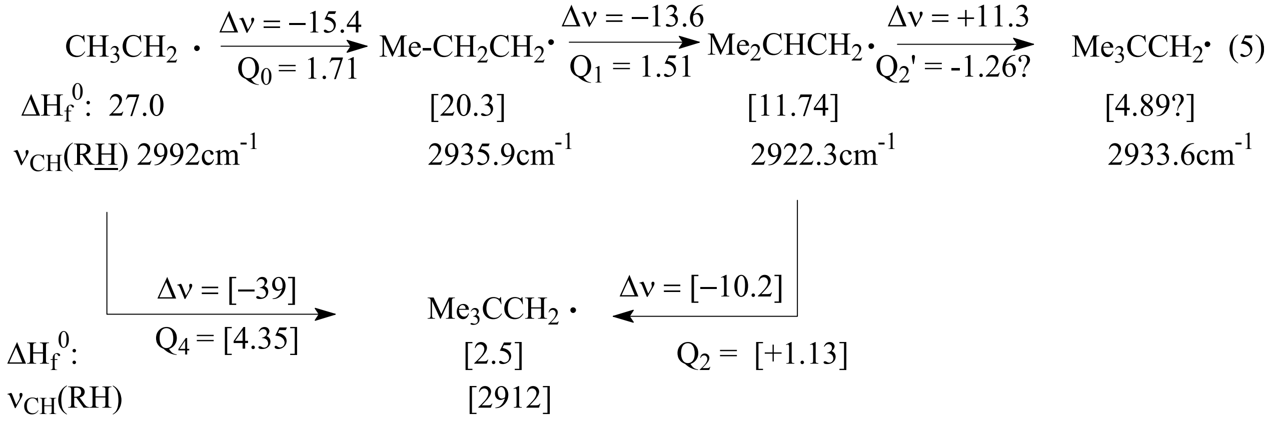
Table. Thermochemical data on $RC\equiv C\bullet$ free radicals and their parent $RC\equiv CH$ molecules

$RC\equiv C\bullet$	$\nu(RC\equiv C\underline{H})$ cm^{-1}	$\Delta\nu(HC\equiv CH \rightarrow RC\equiv C\underline{H})$ cm^{-1}	SE $(HC\equiv C\bullet \rightarrow RC\equiv C\bullet)$	ΔH_f^0 $(RC\equiv C\bullet)$		$\Delta H_f^0(RC\equiv CH)$ [1]
				this work	lit.	
$HC\equiv C\bullet$	3335.6	0.0	0.0	123	see text	54.54 [22]
$CH_3C\equiv C\bullet$	3334.49	-1.11	-0.09	111.56	107.5, 109, 116.3, 123.8, 125.1, 128.6, 143.9	44.2 [22]
$C_2H_5C\equiv C\bullet$	3332	-3.6	-0.3	106.66	101.7	39.5 [22]
$Me_3CC\equiv C\bullet$	3329.37	-6.23	-0.52	92.51		25.57
$HC\equiv CC\equiv C\bullet$	3332.15	-3.45	-0.29	180.17	165.5, 170.7, 186.4, 188.6, 197.5, 201	113
$PhC\equiv C\bullet$	3328	-7.6	-0.63	145.13	153.4, 156.3, 158.2	78.4
$FC\equiv C\bullet$	3357.0	21.36	1.78	75.24	75.5, 83±20, 105.8, 107.8, 108.5, 109.1	6.0
$ClC\equiv C\bullet$	3340.7	5.1	0.43	113.4	114.5, 135.7	45.5
$CF_3C\equiv C\bullet$	3327.3	-8.3	-0.7	-44.24	-25.9	-111
$N\equiv CC\equiv C\bullet$	3327.4	-8.2	-0.69	153	131, 145.6, 149, 150, 158, 169.7, 178.2	86.2
$CNC\equiv C\bullet$	3339	3.4	0.28	174.24		106.5
$F_5SC\equiv C\bullet$	3327.55	-8.05	-0.68	106.86		-175
$Me_3SiC\equiv C\bullet$	3312.46	-23.14	-1.93	69.53		4

It is remarkable that most of the substituents stabilize ethynyl radical compared with unsubstituted one. This can be explained by low thermodynamic stability of HC≡C• radical which extracts stabilization even from such traditionally electron-withdrawing groups as CF_3, NC- or SF_5. Their polarizability effects, which are opposite to their EN effects, come in action [1]. This is supported by the fact that only small (F, Cl, HO) or charged ($^-C≡N^+$-) substituents destabilize HC≡C• free radical.

Negative results and difficulties. Among 25 substituted methanes CH_3X (F, Cl, Br, I, CF_3, CH_2Cl, $CHCl_2$, CCl_3, SH, PH_2, NO_2, ONO_2, CN, C_2H_3, Ph, C≡CH), CH_2X_2 and CHX_3 (X = F, Cl, Br, I) only in case of $C\underline{H}F_3$, $C\underline{H}_3CH_2Cl$, $C\underline{H}_3CHCl_2$, $C\underline{H}_3CCl_3$ and $C\underline{H}_3CF_3$ $\Delta\nu_{C\underline{H}}$ (exp.) (from Refs 1, 6-12) are in consensus with BDE C-H bonds gained from the known ΔH_f^0 values of R• free radicals. In all other cases $\nu_{C\underline{H}}$ (exp.) exceeds ν_{CH} value expected from ΔH_f^0 (R•) (lit.) (when taking $\Delta\nu/\Delta$BDE 9 cm^{-1}/1 kcal mol^{-1}) by 25-189 cm^{-1} or 2.8-21 kcal mol^{-1} in ΔBDE. For some of such molecules ($PhC\underline{H}_3$, CH_2=$CHC\underline{H}_3$, $C\underline{H}_3F$, $C\underline{H}_2F_2$) the explanation of deviation to higher ν_{CH} values is straightforward: the loss in IR spectrum of the band for C-H bond which is trans- to either heteroatom's lone pair (O, N) or to π-system. Such lost band with lowest ν_{CH} belongs to the conformer with lowest BDE, i.e. the less thermodynamically stable conformer in relation to dissociation process. But for the most of the other CH_3X, CH_2X_2 and CHX_3 molecules giving large deviations to higher frequencies one should address, probably, to involvement of "excited" states analogous to those in UV- or electron impact ionization.

When such "excitation" is large it is hardly possible to ascribe the observed ν_{CH} value to the process of formation of R• radical in its ground state. However, when such increase in ν_{CH} value is a small one this value can be treated as responsible for "adiabatic" dissociation leading to calculation of the "true" R• heat of formation. Therefore, all data in ν_{CH} values might be verified using isodesmic reactions like it was done above with CH_3OCH_3 molecule (Eqn 3). Here we give one more example (Eqn 5) (ν_{CH} values – from Ref. 10; ν and Δν in cm^{-1}; ΔH_f^0 and Q – in kcal mol^{-1}; Δν 9 cm^{-1} is taken for equivalent of 1 kcal mol^{-1}; derived values – in square brackets)



We observe the well-known attenuation effect with $Q_1 < Q_2$ (both values >0) at successive introduction of electron-releasing Me-group to yet more stable free radical (compare with Eqn 3 and see Refs 1, 2, 4, 5). Therefore, the rise of ν_{CH} value from $Me_2CHC\underline{H}_3$ to $Me_3CC\underline{H}_3$ by 11.3 cm^{-1} which might indicate destabilization (?) of free radical at H → Me replacement seems strange. Really, such replacement decreases ν_{CH} (Eqns 3, 5 and Table). Taking $Q_2/Q_1 \sim 0.75$ for β-substitution (see above) we obtain Q_2 1.51 x 0.75 = 1.13 kcal mol^{-1} and $\Delta\nu$ (calc.) –10.2 cm^{-1} for $Me_2CHC\underline{H}_3 \rightarrow Me_3CC\underline{H}_3$ which gives ν_{CH}(calc.) in $Me_3CC\underline{H}_3$ 2922 – 10.2 ~ 2912 cm^{-1}. Such band is absent for unknown reasons in IR spectrum of neopentane Me_4C but in Raman spectrum of gaseous and liquid of this substance there are the bands at 2923 and 2912 cm^{-1}, respectively [39].Thus, we gave several examples when the band "missing" in gas-phase IR spectra can be found in Raman spectra of either gaseous or liquid substances. Now we again verify the $\Delta\nu_{CH}$(calc.) for $Me_3CC\underline{H}_3$ 2912 cm^{-1} leading to ΔH_f^0 $Me_3CCH_2\bullet$ 2.5 kcal mol^{-1} (Eqn 5) by isodesmic reaction $Me\text{-}CH_2\bullet + Me_4C \rightarrow C_2H_6 + Me_3CCH_2\bullet + Q$ or brief form: $MeCH_2\bullet \rightarrow Me_3CCH_2\bullet + Q$ (Eqn 6) suggesting diverse literature values for the heat of formation for $Me_3CCH_2\bullet$ free radical (ΔH_f^0 and Q – in kcal mol^{-1})

$$Me\text{-}CH_2\bullet \rightarrow Me_3C\text{-}CH_2\bullet + Q \qquad (6)$$

ΔH_f^0:	27.0	2.5*	+ 4.35
		4.6 [17]	+ 2.25
		4.89**	+1.96
		5.5 [7]	+1.35
		6.7 [40]	+0.15
		8.7 [34]	-1.85
		10.0 [41]	-3.15

*)suggested in this work

**) calculated from ν_{CH}(exp.) in Me_3CCH_3

The value 2.5 kcal mol^{-1} seems to be most reliable since Q 4.35 kcal mol^{-1} corresponding to the three H → Me replacements in β-position stands in line with Q' 6.44 kcal mol^{-1} for $MeCH_2\bullet \rightarrow Me_3C\bullet$ reaction with two H → Me replacements in α-position (Q' comes out of ν_{CH} 2951.3 and 2893.3 cm^{-1} in $MeC\underline{H}_3$ and $Me_3C\underline{H}$ molecules [10], respectively). The small positive, or, even more, negative Q values in Eqn 6 are in obvious conflict with known electron-releasing properties of Me-group [2, 4, 5, 16, 18, 28, 37, 38].

Now we briefly mention other possible sources of errors and difficulties in application of gas phase IR spectra to thermochemistry of free radicals. The first one is the problem of correct ascribing of the experimental bond to namely C-H vibration. The second one is the expected difference between the ν_{CH} of undeuterated and deuterated molecules when ν_{CH}(isolated) frequencies are measured in $–CHD_2$ and –CHD-groups. In this work we claim the importance of EN of carbon atom for the value $\Delta\nu_{CH}$ in, say, CH_2X and CHX_2 groups depending on the EN of X-atom or group. But, we adjust the single value 9 cm^{-1}/1 kcal mol^{-1} to all saturated aliphatic compounds.

Nevertheless, we think that we demonstrated the utility of IR spectra for thermochemistry of free radicals when they are combined with isodesmic reaction control.

Acknowledgment

The authors are thankful to Dr.D.N.Shishkin (Dept. of Physics of St.Petersburg University) for clarification of some problems related to IR spectroscopy.

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Biographies

Aleksander Golovin was born in 1951. From 1969 up to now he was a student, post-graduate and then working as a researcher in a staff of the Department of Photonics in the Faculty of Physics of St.Petersburg University. He is a highly qualified specialist in photoionization and applied mass spectrometry. In this area he worked in laboratories of France, Germany, Britain and USA (Ford Motor Co), and now in Japan.

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Vjatcheslav Takhistov was born in Leningrad (Russia) in 1938. From 1955 up to 1997 he was student, post-graduate, assistant professor, docent in the Faculty of Chemistry of Leningrad (St.Petersburg) University (Departments of Physical Organic Chemistry and Chemistry of Natural Products). From 1997 up to now he is a senior researcher in Academic Research Institute “Center of Ecological Safety” (St.Petersburg). His PhD (1967) and Dr.Sci (1989) dissertations are dedicated to thermochemical description of fragmentation rules for positively and negatively charged ions in mass spectrometer. He is an author of more than 80 publications, including two books (essential part with D.Ponomarev) in organic mass spectrometry, thermochemistry of ions and free radicals, structural elucidation of novel potential ecotoxicants in waters of North-West Russia and Finland. On long-time terms he worked in laboratories of Scotland, Germany, Finland and USA (Ford Motor Co, Dearborn).