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Thermochemistry of Organic and Heteroorganic Species. Part XIV[*]. Application of IR Spectra of the Unsaturated Aliphatic Molecules for Thermochemistry of Vinylic and Allylic Free Radicals

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The application of IR-spectroscopy supplemented by method of isodesmic (formal) reactions which characterize the relative stabilities of free radicals is demonstrated as a useful tool for getting novel data of the enthalpies of formation for certain types of free radicals. In a result, ΔH_f^0 values for 23 $XC(\bullet)=CH_2$ and 17 $XC(\bullet)=O$ novel radicals were obtained and for 8 more drastically corrected from literature ν_{CH} values in $XC\underline{H}=O$ and $XC\underline{H}=CH_2$ molecules, respectively. On the example of $H\text{-}CH_2C(X)=O$ molecules it was demonstrated the possibility to estimate the enthalpies of formation of ground state free radicals from ν_{CH} values for excited C-H bonds. Using the results on the latter radicals the ΔH_f^0 values for 7 novel $\bullet CH_2C(X)=CH_2$ radicals were estimated with the aid of isodesmic reactions. In all these calculations the variable $\Delta\nu_{CH}$ value at H → X replacement equivalent to 1 kcal mol^{-1} in C-H bond dissociation energy was applied: 9 cm^{-1} for $H\text{-}CH_2R$ bond and 11 $^{cm-1}$ for vinylic C-H bond.

The strong destabilization effect in both vinylic type $XC(\bullet)=O$ and $XC(\bullet)=CH_2$ free radicals at H → X replacement (X – substituent with lone pair or π-electrons) was found. For $XC(\bullet)=O$ radicals even with such groups as RO or R_2N, traditionally treated as strong electron-donating, destabilization effect at H → X replacement was demonstrated. The origin of this effect was suggested in the absence of overlapping of free radical center with lone pair or π-electrons of substituent X. Stabilization (destabilization) of vinylic free radicals is found to be the result of electronegativity/polarizability interplay of a substituent.

Keywords. Thermochemistry; free radicals; IR spectra

Abbreviations and notations

BDE, bond dissociation energy
EN, electronegativity
PAZ, polarizability
PI MS, photoionization mass spectrometry
SE, stabilization energy

INTRODUCTION

Recently the systematic application of known $\nu_{C\text{-}H}$ frequences from gas phase IR spectra of R-H molecules to checking, correcting or finding novel values of the enthalpies of formation for corresponding R• free radicals has been demonstrated [1-4]. These works followed the fundamental works of McKean with collaborators [5-10] who had shown that Δν (R-H → R'-H) values were correlated with ΔBDE (bond dissociation energies), i.e. [BDE(R-H) → BDE(R'-H)] values in molecules and consequently with the enthalpies of formation for corresponding R• and R'• free

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radicals. The problems arising in these correlations are discussed in details in Refs 1-10. For such correlations McKean suggested to take *unique* value in $\Delta\nu$ about 11.5 cm^{-1} for $R\underline{H} \rightarrow R'\underline{H}$ replacement equivalent to 1 kcal mol^{-1} for ΔBDE in R-H → R'-H molecules [5, 6]. Conversely, we showed that the *variable* $\Delta\nu$ equivalents to 1 kcal mol^{-1} in ΔBDE, depending roughly on electronegativity (EN) of C-atom, better fitted such interrelationships [1-4]. Finally, 9 cm^{-1} in alkanes, 11 cm^{-1} at H-C=C double bond, 12 cm^{-1} at H-C≡C triple bond and 14 cm^{-1} in RC(-H)=O molecules for $\Delta\nu$ values were adjusted to 1 kcal mol^{-1} in ΔBDE values [1,3,4].

In present work we further explored these correlations to find out novel values of the enthalpies of formation for RC(•)=O, $R'C(\bullet)=CH_2$ and some $\bullet CH_2C(X)=CH_2$ free radicals. To find out these values we applied the well known equation suggested by Benson as early as in 1965 for quantitative evaluation of the relative stabilities E_s of free radicals (Eq.1) [11].

$$E_s = \Delta H_f^0(R\bullet) + \Delta H_f^0(R_1H) - \Delta H_f^0(RH) - \Delta H_f^0(R_1\bullet) \qquad (1)$$

For our purpose, estimation of the enthalpies of formation for free radicals, we apply Eq.1 in the form of isodesmic (formal) reaction (Eq.2, where $Q = E_s$)

$$R\bullet + R_1H \rightarrow RH + R_1\bullet + Q \qquad (2)$$

The full form of this formal reaction incorporating the ΔH_f^0 values of all participants of the reaction is given by Eq.3

$$\Delta H_f^0(R\bullet) + \Delta H_f^0(R_1H) \rightarrow \Delta H_f^0(RH) + \Delta H_f^0(R_1\bullet) + Q\ (= E_s) \qquad (3)$$

To obtain the ΔH_f^0 value of the target $R_1\bullet$ from that of model free radical $R\bullet$ we apply Eq.4 coming out from Eq.3

$$\Delta H_f^0(R_1\bullet) = \Delta H_f^0(R\bullet) - \Delta H_f^0(RH) + \Delta H_f^0(R_1H) - Q \qquad (4)$$

The obvious advantage of the use of isodesmic reactions to compare the *relative* stabilities of free radicals is the exclusion of the enthalpies of formation for molecules, i.e. free radicals' skeletons and leaving only the enthalpy Q of stabilization (Eq.3, $Q>0$) or destabilization (Eq.3, $Q<0$) of the target $R_1\bullet$ compared with the model $R\bullet$ free radical. Such way of comparison of free radicals relative stabilities is very convenient and easily perceptible. Q value expresses the deviation of the resulted $\Delta H_f^0(R_1\cdot)$ value from additive scheme thus making doubtful the elaboration of group contributions for free radicals which still appear in the literature (for example, Refs. 12 and 13).

SUBSTITUTED CARBONYL XC(•)=O FREE RADICALS

We begin presentation of $\Delta\nu$/BDE ($=\Delta\Delta H_f^0$) correlations from a representative set of $RC\underline{H}=O$ molecules (Table 1) (for ΔH_f^0 values of molecules see Appendix). To extract the enthalpies of formation for free radicals RC(·)=O we applied the following calculation scheme based on Eq.4 and literature $\nu_{CH}(RC\underline{H}=O)$ values in gas phase IR spectra. Formaldehyde H-CH=O was taken as a

Table 1. Thermochemical characteristics of RC(•)=O free radicals (ν_{CH} values in cm^{-1} – from Refs. 5 and 6, ΔH_f^0 and Q – in kcal mol^{-1}, derived values – in square brackets)

X-CH=O	ν_{CH}	ΔH_f^0 (RH)	$\Delta\nu(H\to X)$	Q $H\to X$	ΔH_f^0 R• calc. from $\Delta\nu$	final	ΔH_f^0(R•) lit.
$Me_2C=CH$	2768 [15]	[-35.5]	-45	3.21	-2.7	-2.5	
Me	2770	-39.73	-43	3.07	-6.8	-6.8	-2.4 [12], -4.5 [13], -5.4 [14, 19]
Ph	2770	-8.8	-43	3.07	24.1	24	26.1 [13, 14], 27.8 [12]
H	**2813**	-26.0	0.0	0.0	10.0		9.96 [12], 10.0 [13]
MeS	2838 [16]	[-33.5]	25	-1.8	4.3	4.5	
HS	[2844]	-30	31	-2.2	8.2	8.0	
CF_3	2844	-188.3	31	-2.2	-151.1	-151	-128.4 [12]
Me_2N	[2844]	-45.8	31	-2.2	-6.0	-6.0	
Br_3C	2845	[-1]	32	-2.3	-38.0	-38	
MeNH	[2847]	[-44.5]	34	-2.4	-5.5	-5.5	
CHO	2850	-50.7	37	-2.6	12.1	12	
H_2N	2852	[-43.5]	39	-2.8	-4.7	-4.5	
Cl_3C	2856	[-38.1]	43	-3.1	1.0	1	
$HC\equiv C$	2858	24.5	45	-3.2	64.4	64.5	
$BrC\equiv C$	2858 [16]	[28]	45	-3.2	67.9	68	
$ClC\equiv C$	2860 [16]	[15.5]	47	-3.36	55.4	55.5	
Br	2912.5 [17]	[-32.5]	99.5	-7.1	10.6	10.5	
I	2930 [17]	-17	117	-8.36	27.8	28	
MeO	2930	-85.0	117	-8.36	-40.2	-40	-40.4 [19]
Cl	2934 [17]	[-45]	121	-8.64	-0.5	-0.5	-2.8 [13], -5.2 [13]

HO	2943	-90.5	130	-9.3	-45.9	-45	-46.5 [12], -47.3 [20] , -53.3 [13]
HCOO (two rotamers)	2948 [18] 2964 [18]	[-110]	135 151	-9.6 -10.8	-63.9 -62.7	-64	
F	2981.2 [17]	[-93]	168.2	-12.0	-44.4	-44.5	-43.0 [13]

model compound. The ΔH_f^0 HC(·)=O 10.0 kcal mol^{-1} is well established [12, 13]. We give an example of calculation for ΔH_f^0 MeC(·)=O free radical from ν_{CH} MeC$\underline{H}$=O molecule. ΔH_f^0 [MeC(·)=O] = ΔH_f^0[HC(·)=O] - ΔH_f^0(H_2C=O) + ΔH_f^0(MeCH=O) – Q = 10.0 – (-26.0) + (-39.73) – Q = -3.73 kcal mol^{-1} – Q (Eq.4, R = H, Me). We gain Q = {[ν_{CH}(H-CH=O)- ν_{CH}[CH_3C(-H)=O]}: 14 = (2813 – 2770): 14 = 43:14 = 3.07 kcal mol^{-1}. Each 14 cm^{-1} in $\Delta\nu$ are equivalent to 1 kcal mol^{-1} in Δ ΔH_f^0 values. The positive sign of Q 3.07 signifies that acetyl CH_3C(·)=O is by 3.07 kcal mol^{-1} more stable than formyl HC(•)=O free radical or, in other words H → CH_3 replacement reveals stabilization of free radical center by 3.07 kcal mol^{-1}. Thus, in general, we use the additive scheme but untroduce correction term Q reflecting quantitatively the electron-donating (Q>0) or electron-withdrawing (Q<0) properties of R-substituent compared with H-atom in formyl H-C(·)=O radical. ν_{CH} values for some molecules were extrapolated using IR data for structurally close compounds, like HSC$\underline{H}$=O from data on MeSC$\underline{H}$=O or MeNHC$\underline{H}$=O and $Me_2NC\underline{H}$=O from data on $H_2NC\underline{H}$=O molecule keeping in mind that H → Me replacement decreases the ν_{CH} value which parallels the decrease of the BDE C-H in molecules.

Analysis of data collected in Table 1 revealed some unexpected features. The first of them is the minor (if any) role of resonance (conjugation) interaction of lone pairs of heteroatom or π-system (Ph, XC≡C) with unshared electron at free radical center. Such substituents as halogens and especially RO-, RS-, R_2N (R = H, alkyl)-groups, being well known as stabilizing free radical center compared with Me-group, reveal, contrary, the destabilizing effect in the RC(·)=O series. Let us compare the Q values (Table 2) for two isodesmic reactions Eqs 5 and 6. The data for RCH_2· radicals are taken from Ref.14 (here ΔH_f^0 for CH_3· radical is taken 35.1 kcal mol^{-1}) and for RC(·)=O radicals from present work. The isodesmic reactions in Table 2 are given in a brief form like CH_3· → ·CH_2NMe_2 + Q, instead of a full form (Eqs 5 and 6) or CH_3· + CH_3NMe_2 → CH_4 + ·CH_2NMe_2 + Q_1.

$$CH_3\cdot + XCH_3 \rightarrow CH_4 + XCH_2\cdot + Q_1 \qquad (5)$$

$$HC(\cdot){=}O + XCH{=}O \rightarrow H_2C{=}O + XC(\cdot){=}O + Q_2 \qquad (6)$$

All substituents collected in Table 2 stabilize CH_3· free radical (Q_1 > 0) while in substituted formyl XC(·)=O free radicals only Me- and Ph-groups reveal a small stabilizing effect (Q_2 > 0). Even such traditionally very strong electron donating groups as H_2N-, -OMe, MeNH-, Me_2N-

Table 2. Stabilization energies Q for $CH_3\bullet \rightarrow XCH_2\bullet$ (Q_1) and $HC(\bullet)=O \rightarrow XC(\bullet)=O$ (Q_2) (ΔH_f^0 R• and Q – in kcal mol^{-1}); ΔH_f^0 ($\bullet CH_2X$) from Ref. 4, ΔH_f^0 $XC(\bullet)=O$ – this work (Table 1)

$\bullet CH_2X$	$\Delta H_f^0(\bullet CH_2X)$	Q_1	$XC(\bullet)=O$	Q_2
$CH_3\bullet \rightarrow \bullet CH_2NMe_2$	25.8	21.4	$HC(\bullet)=O \rightarrow Me_3NC(\bullet)=O$	-2.2
$\rightarrow \bullet CH_2NHMe$	30.9	17.5	$\rightarrow MeNHC(\bullet)=O$	-2.4
$\rightarrow \bullet CH_2NH_2$	34.9	12.5	$\rightarrow H_2NC(\bullet)=O$	-2.8
$\rightarrow \bullet CH_2OMe$	-5.0	13.9	$\rightarrow MeOC(\bullet)=O$	-8.4
$\rightarrow \bullet CH_2OH$	-3.2	7.9	$\rightarrow HOC(\bullet)=O$	-9.3
$\rightarrow \bullet CH_2F$	-7.5	6.1	$\rightarrow FC(\bullet)=O$	-12
$\rightarrow \bullet CH_2Cl$	28.5	4.8	$\rightarrow ClC(\bullet)=O$	-8.6
$\rightarrow \bullet CH_2Br$	41	2.3	$\rightarrow BrC(\bullet)=O$	-7.0
$\rightarrow \bullet CH_2I$	54.5	1.3	$\rightarrow IC(\bullet)=O$	-8.4
$\rightarrow \bullet CH_2Me$	27	5.8	$\rightarrow MeC(\bullet)=O$	3.1
$\rightarrow \bullet CH_2Ph$	47	17.9	$\rightarrow PhC(\bullet)=O$	3.1

destabilize formyl radicals ($Q_2 < 0$). All that signifies that in substituted formyl free radicals there is no overlapping between heteroatoms' lone pair and unshared electron of free radical center or, in other words, the conjugation between them is absent. If in the series of halogeneted $XCH_2\bullet$ radicals the resonance stabilization decreases in the row F > Cl > Br > I in consensus with their R^+ values –0.52 (F), –0.31 (Cl), –0.30 (Br) and –0.28 (I) [21] the observed effect in halogenated formyl radicals is the opposite one just following inductive σ_I [21] or electronegativity values [3]. Thus, it may appear that substituted formyl radicals may become the models of "pure" inductive effect without involvement of resonance effect.

Another interesting observation is that electron-donating effects of Me- and Ph-groups are identical in their relation to stabilization of formyl free radical while, as expected, the latter demonstrated the much higher substitution effect on $XCH_2\bullet$ radical when compared with X = Me. This again can only be treated as the evidence of absence of resonance stabilization of the free radical center by π-system while minor stabilization still takes place owing to polarizability (PAZ) effect of Ph- which is expected to be larger than with Me-group (compare ENs values 4.8 and 5.4 units for Me- and Ph-groups, respectively [3]).

One more specific feature of the $XC(\bullet)=O$ system is contribution of PAZ effect of X-substituents. Its role in stabilization of free radicals on the example of $XC\equiv C\bullet$ species is described in detail in Ref.3. It is expected that the larger is the size of an atom or of a group the larger is the

PAZ effect inspired by electron-deficient free radical center. The behavior of XC(•)=O radicals (Tables 1 and 2) parallels that observed with XC≡C• free radicals. For the latter only a few "hard" (of small size and low PAZ) substituents F, HO, Cl, and –N=C destabilize HC≡C• radical in the framework of isodesmic reaction HC≡C• + XC≡CH → HC≡CH + XC≡C• + Q (Q<0). All others, including such traditionally treated as strong electron-withdrawing groups as -C≡N, CF_3, COOH and even SF_5 stabilize XC≡C• radical (Q>0) since ν_{CH} values for XC≡C-H molecules with these groups are *lower* than ν_{CH} for unsubstituted HC≡CH molecule [1,3].

Since HC(•)=O radical is much more stable [by 32.5! kcal mol^{-1}(=Q^0)] in the framework of isodesmic reaction HC≡C• + CH_2=O → HC≡CH + HC(•)=O + Q^0 many other X-atoms and groups enter the list of destabilizing substituents. This comes out from our observations and found regularities that some substituents stabilize unstable, like Me• radicals while destabilize the more stable radicals like Me_2CH•, that is Q>0 for Me• + CH_3X → MeH + •CH_2X and Q<0 for Me_2CH• + Me_2CHX → Me_2CH_2 + Me_2C(•)X isodesmic reaction. In the absence of possibility to bring about their resonance effect in XC(•)=O system such substituents as halogens, RO-, RS-, RC≡C- and even R_2N- exhibit electron-withdrawing (destabilizing) effects. Of course, one should not expect to "measure" the PAZ effect directly from IR data since the interplay between EN and PAZ of a group might appear to be very complex [3]. For example, such rather diverse groups as CF_3, CBr_3, HS, Me_2N or Cl_3C and HC≡C give very close ν_{CH} values. Another complicating factor even in case of structurally close groups like CX_3 (F, Cl, Br) is the possible difference in their geometrics in relation to C-H bond in RC$\underline{H}$=O molecule.

1-X-SUBSTITUTED VINYL FREE RADICALS

For XC$\underline{H}$=CH_2 molecules and XC(•)CH=CH_2 free radicals the effects similar to those for XC$\underline{H}$=O molecules and XC(•)=O radicals, respectively, are expected. The set of compounds XC$\underline{H}$=CH_2 for which the data on IR spectra are available is more narrow owing to chemical instability of many of them like XCH=CH_2 with X=OH, SH, NH_2. Still, the general tendencies in structure/enthalpy of formation are similar in both classes of compounds. The most important and common tendency remains untouched, this is the minor (if any) participation of resonance (conjugation) effect in interaction of X-substituent, possessing either lone pairs or π-electrons, with free radical center and the important role of polarizability effect (Table 3). The best example to demonstrate the role of PAZ effect are the ν_{CH} values for CH_2=$CHEH_2$ molecules, where E is the element of V (15) group N-Bi (Table 3).

Vinyl •CH=CH_2 radical is by 21.55 kcal mol^{-1} less stable than •CH=O free radical in the framework of isodesmic reaction •CH=O + CH_2=CH_2 → CH_2=O + •CH=CH_2 + Q [Q = ΔH_f^0(•CH=O) + ΔH_f^0(CH_2=CH_2) - ΔH_f^0(CH_2=O) - ΔH_f^0(•CH=CH_2) = 10.0 + 12.55 – (-26.0) –70 = = -21.55 kcal mol^{-1}(destabilization)]. Therefore, many of the substituents which destabilize the XC(•)=O free radicals now become stabilizing ones in XC(•)=CH_2 radicals in the framework of

Table 3. Thermochemistry of XC(•)=CH_2 free radicals [ν_{CH} and Δν - in cm^{-1} refer to vinylic C-H bond), ΔH_f^0 and Q values – in kcal mol^{-1}, derived values – in square brackets; for ΔH_f^0 of parent molecules see Appendix]

X-C<u>H</u>=CH_2	ν_{CH}	ΔH_f^0 XCH=CH_2	Δν(H→X)	Q H→X	ΔH_f^0 XC(•)=CH_2		literature value
					from Δν	final	
H_2Bi	[2940]	[75]	-120	11.0	121.5	121.5	
H_2Sb	2949.3[22]	[57.7]	-110.7	10.1	105.14	105	
H_2As	2959[22]	[35.5]	-101	9.2	83.8	84	
Me_2N	[2975]	[13]	-85	7.7	62.9	63	
H_2P	[2980]	[19.8]	-77	7	70.5	70.5	
MeNH	2990[23]	[14.2]	-70	6.4	65.3	65.5	
ClCO (two rotamers)	2990[24] 2998	[-32]	-70	6.4	19.3	19.5	
CH_3CO	[2997]	[-28]	-63	5.7	23.6	23.5	27 [20]
Et	2998[16]	0.02	-62	5.6	51.8	52	
CH_2=CH	3000[25]	26.3	-60	5.5	78.2	78	
Ph	[3000]	35.35	-60	5.5	87.2	87	74 [20]
Me	3001[5]	4.88	-59	5.4	56.7	56.5	
H_2N	[3010]	13.5	-50	4.5	66.3	66.5	57.5 [20]
HC≡C	3012[5]	69.8	-48	4.4	122.7	122.5	108 [29]
$ClCH_2$	3021[16]	0.5	-39	3.5	54.2	54	
$BrCH_2$	3021[16]	10.8	-39	3.5	64.7	64.5	
FCH_2	3026[16]	-35.5	-34	3.1	25.1	25	
MeS	3044[25]	[16]	-16	1.5	72.0	72	
Cl_2C=C(Cl)	3047[27]	11.5	-13	1.2	67.7	67.5	
H	**3060**[5]	12.55	0.0	0.0	70.0	70	
MeO	3065[5]	[-24.5]	5.0	-0.6	33.5	33.5	
HS	[3070]	19.5	10	-0.9	78.0	78	

CF_3	[3070]	-151	10	-0.9	-92.5	-92.5	
Cl	3071[28]	5.2	11	-0.9	63.3	63.5	
N≡C	3078[5]	43.16	18	-1.6	102.2	102	
F	3080[5]	-35	20	-1.8	24.4	24.5	
HO	[3082]	-30.4	22	-2.0	28.9	29	17.5 [20]
Br	3085[5]	18	25	-2.3	77.8	78	
I	[3087]	32	27	-3.5	91.9	92	

isodesmic reactions. In other words, the less stable vinyl $\bullet CH{=}CH_2$ free radical extracts stabilization from those substituents which in the system of more stable formyl $\bullet C(H){=}O$ radical were electron-withdrawing, i.e. destabilizing the latter ones. This fact stands in line with our previous observations (see above and Refs.1-4,14). Among those which now destabilize vinyl radicals we find all halogens, HO, MeO, HS and NC-groups. Using the known experimental data we – by interpolation – ascribed ν_{CH} values for some $XC\underline{H}{=}CH_2$ molecules for which such data are not available. IR spectra of substituted ethylenes $XCH{=}CH_2$ revealed certain specificity in interaction of halogens with π-double bond. The measured ν_{CH} values in the series of halogenated ethylenes $XCH{=}CH_2$ (F, Cl, Br, I) range only for 7 cm^{-1} (compare with the range of 70 cm^{-1} for $XC\underline{H}{=}O$ molecules – see above) (Table 3). Thus, it is hardly possible to make any definite conclusions about the role of inductive effect (or EN), polarizability and geometrical fine structure for a particular halogen.

Summarizing the data on thermochemistry of free radicals of vinylic type we now realize that our earlier estimations of the enthalpies of formation of some $XC(\bullet){=}CH_2$ radicals (X = Ph, H_2N, HO, HC≡C) [20,29] (Table 3) were based on erroneous assumptions that either of free radicals saturated and vinylic ones follow similar structure/stability interrelationships. Similarly, the quoted value for ΔH_f^0 $CF_3C(\bullet){=}O$ radical –128.4 [12] compared with the value –151 kcal mol^{-1} (present work) would give unprobably high destabilization effect of –23.6 kcal mol^{-1} for $HC(\bullet){=}O \rightarrow CF_3C(\bullet){=}O$ replacement (compare with –2.2 kcal mol^{-1} – Table 1). This would lead to unprecedented value for ν_{CH} in $CF_3C\underline{H}{=}O$ molecule being much more higher than with F-substituent: $\nu_{CH}(CF_3CH{=}O) = \nu_{CH}(CH_2{=}O)(2813) + 23.6 \times 14$ (see above) = 3143.4 cm^{-1}(?).

ALLYLIC TYPE $\bullet CH_2C(X){=}O$ FREE RADICALS

According to Ref.6 $C\underline{H}_3CHO$ molecules exhibit in its IR spectrum two bands with ν_{CH} frequencies in CH_3-group 2945 (CH_{as}) and 3002 (CH_{sym}). The lower ν_{CH} (antisymmetric or cis) corresponds to free radical's conformer $\bullet CH_2CH{=}O$ in which free radical's center practically does not interact with the double C=O bond. The higher ν_{CH} (symmetric or trans) belongs to the conformer in which free radical's electron is actively interacting with this double bond performing the destabilizing effect since here CO-group reveals its electron-withdrawing properties. However, even the lower ν_{CH} corresponds to $\bullet CH_2CH{=}O$ radical being in "excited" rather in its ground state. According to McKean [6] BDEs $H\text{-}CH_2CH{=}O$ are 99.4 and 92 kcal mol^{-1}, coming, respectively, from ν_{CH} 2945 cm^{-1} value and from kinetic data (ground state). Thus, all low ν_{CH} values in $H\text{-}CH_2C(X){=}O$ molecules (Table 4) correspond to formation of $\bullet CH_2C(X){=}O$ radical in "excited" state with cis-position of unshared electron to CO-group. We estimated the ehthalpies of formation of series of $\bullet CH_2C(X){=}O$ radicals applying the known ΔH_f^0 value for unsubstituted $\bullet CH_2CH{=}O$ 3 kcal mol^{-1} (kinetic and mass spectrometric studies [14]) by estimating ν_{CH} $H\text{-}CH_2C(X){=}O$ in the ground state with the help of following equations (ΔH_f^0 and Q – in kcal mol^{-1})

Table 4. Thermochemistry of $\bullet CH_2C(X){=}O$ free radicals (ν_{CH} from Ref. 6 - in cm^{-1}); ΔH_f^0 and Q values – in kcal mol^{-1}; molecules' ΔH_f^0 – from Ref. 31; derived values – in square brackets)

Molecule RH	ΔH_f^0 RH	$\nu_{exp.}$ CHas	$\nu_{calc.}$ CHas	Q_0 H→X	ΔH_f^0 $\bullet CH_2COX$	$\nu_{exp.}$ CHsym	Q_1 H→X	ΔH_f^0 $\bullet CH_2COX$
$C\underline{H}_3CH{=}O$	-39.73	2945	2900.5	0.0	3.0[a]	3002	0.0	9.3
$C\underline{H}_3COCH_3$	-51.94	2946	2893.5	-0.1	-9.1[a], -10[b]	3004	-0.2	-2.7
$C\underline{H}_3COF$	-105.66	2980.1	2935.6	-3.9	-59[a], -60.5[b]	3025.4	-2.6	-54
$C\underline{H}_3COCl$	-58.3	2978.5	2934	-3.8	-11.5[a], -14[b]	3004.0	-0.2	-8.8
$C\underline{H}_3COBr$	-45.5	2978.2	2933.7	-3.7	1.0[a], -1.2[b]	2994.9	0.8	2.7
$C\underline{H}_3COI$	-30.2	[2978]	2933.5	-3.7	16[a]	2983.3	2.1	16.8
$C\underline{H}_3COOMe$	-98.45	2972.7	2928.2	-3.0	-52.5[a], -52.4[b]	3012	-1.1	-48.3
$C\underline{H}_3COCN$	[-3]	2957.5	2913	-1.44	40[a]	3010	-0.9	46

a) this work; b) from Ref. 30

$$CH_3\bullet + CH_3CH{=}O \rightarrow CH_4 + \bullet CH_2CH{=}O + Q_1 \qquad (7)$$

$$\Delta H_f^0 \quad 35.1 \qquad -39.73 \qquad -17.78 \qquad 3 \qquad 10.17$$

$$\nu_{CH}\,(calc.)\ (H\text{-}CH_2CH{=}O) = \nu CH(CH_3\text{-}H) - Q_1(CH_3\bullet \rightarrow \bullet CH_2CH{=}O) \times 9 =$$

$$= 2992 - [10.17 \times 9 = 91.5] = 2900.5 \qquad (8)$$

$$\nu_{CH}(calc. \rightarrow exp.) = 2900.5 - 2945 = -44.5\ cm^{-1} \qquad (9)$$

where 9 cm^{-1} is the equivalent for 1 kcal mol^{-1} in BDEs in $H\text{-}CH_2$-group. Then we calculated ν_{CH} values for the ground states of all other $H\text{-}CH_2C(X){=}O$ molecules using ν_{CH} (exp.) and introducing the common correction term –44.5 cm^{-1} (Eq.9) as for unsubstituted H-CH_2CH=O molecule (Eqs.7-9). For example,

ν_{CH}(calc.) [H-CH_2C(F)=O] = ν_{CH}(exp.) [H-CH_2C(F)=O] (2980.1) – 44.5 = 2935.6 cm^{-1} (10)

From these ν_{CH} (calc.) values for ground state •CH_2C(X)=O radicals with cis-position of unshared electron and CO-group (Table 4) we then calculated the Q values for isodesmic reactions •CH_2CH=O → •CH_2C(X)=O (brief form). For example, ΔH_f^0 [•CH_2C(F)=O] = ΔH_f^0 [•CH_2CH=O] - ΔH_f^0 [CH_3CH=O] + ΔH_f^0 [CH_3C(F)=O] – Q{[ν_{CH}(calc.) H-CH_2C(F)=O] : 9} = 3.0 – (-39.73) – 105.66 [31] – [(2900.5 –2935.6) : 9] = -59.03 ~ 59 kcal mol^{-1} (Eq.11) (Table 4).

When similar calculation was performed with ν_{CH}(sym.) values (Table 4) which were responsible for interaction of CO-group and unshared electron being in trans-position to each other such interaction appeared to be rather specific. Halogens showed the yet higher contribution of their PAZ effects to such an extent that only F-atom (very low PAZ) destabilized •CH_2C(F)=O radical compared with unsubstituted •CH_2CH=O free radical (Q = -2.6), •CH_2C(Cl)=O demonstrated similar stability with the latter (Q = -0.2) while Br- and then I-atoms showed the yet stronger stabilization effects (Q>0). Consequently, for Br- and, especially, for I-substituents both conformers (with either cis- or trans-position of C(X)=O group to unshared electron) become close in their stabilities: compare ΔH_f^0 values for cis- and trans-radicals 1.0 and 2.7 (Br) or 16 and 16.8 kcal mol^{-1} (X = I). We stress that either ν_{CH}(as) or ν_{CH}(sym) values correspond to free radicals being in “excited” states.

Owing to essentially different interaction in cis- and trans-conformers (compare Q_0 and Q_1 – Table 4) it is hardly possible to calculate the ΔH_f^0 values of the trans-substituted radicals in their ground states as it was performed for cis-conformers (see above). All these observations coming from data on IR spectra enlighten the possible complexity in interpretation of experimental results on determination of BDEs in H-CH_2C(X)=O [and H-CH_2C(X)=CH_2 – see later] molecules by methods of chemical kinetics which hardly take in account the described effects coming from IR data.

It is important to mention that experimental ΔH_f^0 values for •CH_2COCH_3 (-10) and •CH_2COOCH_3 (-52.4 kcal mol^{-1}) were obtained by photoionization mass spectrometry (PI MS) [30] (Table 4) and are very close to data gained in present work from IR data thus supporting our methodology of calculating ΔH_f^0 •CH_2C(X)=O free radical from ν_{CH} values related to “excited” C-H bonds. The literature values for •CH_2C(X)=O radicals (F, Cl, Br) were calculated by additive scheme from experimental data on •CH_2C(X)=O radicals (Me, OMe) [30]. We think that ΔH_f^0 •CH_2COCH_3 –10 kcal mol^{-1} gained from PI MS [30] is more reasonable than that obtained from IR spectrum of acetone (Table 4) –9.1 [6] or from chemical kinetics –5.7 [19] kcal mol^{-1}. What is strange that both ν_{CH} values for acetone 2946 and 3004 cm^{-1} are higher than for CH_3CHO molecule 2945 and 3002 cm^{-1}, respectively (Table 4). H → Me replacement might stabilize free radical and thus it is expected that ν_{CH} values should be lower for acetone H-CH_2COCH_3 than for acetaldehyde H-CH_2CHO like it was observed for many other systems at H → Me replacement (Refs 1-4 and Tables 1-3). The possible source of this discrepancy is involvement of the enol form of acetone $CH_2{=}C(OH)CH_3$ molecule. Another possible reason is that namely acetone (for unknown reason) deviates from ν_{CH}(as) (exp. → calc.) tendencies which are followed by all other $CH_3C(X){=}O$ molecules. Still the data on $\bullet CH_2COCH_3$ radical coming from IR spectra and from PI MS differ by only 1 kcal mol^{-1}.

The discrepancy between PI MS and kinetic data –10 [30] and –5.7 [19] kcal mol^{-1}. respectively, can now be explained by involvement in kinetic experiment (bimolecular reaction $X\bullet$ + H-$CH_2COCH_3 \rightarrow HX + \bullet CH_2COCH_3$) of the stronger C-H bond of trans conformer (see above).

ALLYLIC TYPE $\bullet CH_2C(X){=}CH_2$ FREE RADICALS

To derive the enthalpies of formation for this type of free radicals we followed the tendencies in structure/ΔH_f^0 for $\bullet CH_2C(X){=}O$ radicals (see above). In the framework of isodesmic reactions $\bullet CH_2CH{=}CH_2$ is by 8.4 kcal mol^{-1} *more* stable than $\bullet CH_2CH{=}O$ free radical (Eq.12) (ΔH_f^0 and Q – in kcal mol^{-1})

$$\begin{array}{lccccccccc} & \bullet CH_2CH{=}O & + & CH_3CH{=}CH_2 & \rightarrow & CH_3CH{=}O & + & \bullet CH_2CH{=}CH_2 & + & Q \qquad (12) \\ \Delta H_f^0 & 3.0 & & 4.78 & & -39.73 & & 39.1 & & +8.41 \end{array}$$

Since all X-substituents (with exception of Me) destabilize $\bullet CH_2C(X){=}O$ free radicals at H → X replacement, i.e. Q<0 for $\bullet CH_2CH{=}O \rightarrow \bullet CH_2C(X){=}O$ isodesmic reaction (brief form) (Table 4) the same X-substituents will even more destabilize the more stable (Eq.12) allyl $\bullet CH_2C(X){=}CH_2$ free radicals at H → X replacement in β-position to free radical center (see above). We can estimate approximately the Q value for, say, $\bullet CH_2CH{=}CH_2 + CH_3C(F){=}CH_2 \rightarrow CH_3CH{=}CH_2 + \bullet CH_2C(F){=}CH_2 + Q$ isodesmic reaction (Eq.13) applying the known data for less stable $FCH_2CH_2\bullet$ [32] and $\bullet CH_2C(F){=}O$ (this work) free radicals (Eq.14) [the values at arrows signify Q values (in kcal mol^{-1}) for corresponding isodesmic reaction like $\bullet CH_2CH{=}CH_2 \rightarrow \bullet CH_2C(F){=}CH_2$ (brief form) while Eq.13 is the full form of this reaction].

$$\begin{tikzcd} CH_3CH_2\cdot \arrow[r, "+4.3", "Q'"'] \arrow[d, "Q_1"', "-2.7"] & \cdot CH_2CH{=}O \arrow[r, "+8.3", "Q'"'] \arrow[d, "Q_2"', "-3.9"] & \cdot CH_2CH{=}CH_2 \arrow[d, "Q_1"', "{[-5.7]}"] \\ FCH_2CH_2\cdot \arrow[r, dashed, "-1.2"] & \cdot CH_2C(F){=}O \arrow[r, dashed, "{[-1.8]}"] & \cdot CH_2C(F){=}CH_2 \end{tikzcd} \qquad (14$$

Here we applied the earlier found observation that introduction of an electron-withdrawing substituent to yet more stable free radical performs yet higher destabilizing effect (see above). The final values of the enthalpies of formation for $\bullet CH_2C(X){=}CH_2$ free radicals are collected in Table 5.

Table 5. Thermochemical characteristics of •$CH_2C(X)=CH_2$ free radicals (ΔH_f^0 and Q – in kcal mol^{-1}; derived values – in square brackets)

X	ΔH_f^0	Q(H→X)	ΔH_f^0(R•)
H	4.88	0.0	39.1[14]
F	[-46.5]	-5.7	-7.5
Cl	[-5.0]	-5.55	33.5
Br	[8.5]	-5.35	47.5
I	[23.5]	-5.35	61.5
CN	[32]	-2.45	70
MeO	[-35]	-4.15	2.5
HO	[-41.5]	-5.55	-4.5

CONCLUSIONS

In present work we further demonstrated the application of IR spectroscopy as a useful tool for getting novel data of the enthalpies of formation for certain types of free radicals if IR data are supplemented by series of isodesmic (formal) reactions. In a result, ΔH_f^0 values for 23 $XC(•)=CH_2$ and 17 XC(•)=O novel radicals were obtained and for 8 more were drastically corrected using literature ν_{CH} values in $XC\underline{H}=O$ and $XC\underline{H}=CH_2$ molecules. For the first time, on the example of H-$CH_2C(X)=O$ molecules the IR ν_{CH} values for excited C-H bonds were applied to calculate the ΔH_f^0 values in the ground state. Using the results on the latter radicals the enthalpies of formation for 7 novel •$CH_2C(X)=CH_2$ radicals were estimated with the aid of isodesmic reactions.

The strong destabilization effect in both types XC(•)=O and $XC(•)=CH_2$ free radicals at H → X replacement (X – substituent with lone pair or π-electrons) was demonstrated. The origin of this effect was explained by the absence of overlapping of free radical center with lone pair or π-electrons of X-substituent.

Appendix

Most of the known values for the enthalpies of formation for parent molecules are taken from Ref. 31. The values for ΔH_f^0 of $H_2NCH=CH_2$ (13.5), $HSCH=CH_2$ (19.5), $BrCH=CH_2$ (18), $HOCH=CH_2$ (-30.4), $ClCH=CH_2$ (5.2), $CF_3CH=CH_2$ (-151), $FCH=CH_2$ (-35), $FCH_2CH=CH_2$ (-35.5), $ClCH_2CH=CH_2$ (0.5) we extracted from Ref. 32. ΔH_f^0 CF_3CHO –188.kcal mol^{-1} was earlier obtained in Ref. 33. ΔH_f^0 HSCHO –30 kcal mol^{-1} was earlier estimated in Ref. 20 and hence ΔH_f^0 [MeSCHO] = ΔH_f^0[HSCHO] - ΔH_f^0 [MeSH] (-5.5) + ΔH_f^0[MeSMe](-9.0) = -33.5 kcal mol^{-1}. The data for MeNHCHO (or $MeNHCH=CH_2$) and Me_2NCHO (or $Me_2NCH=CH_2$) were estimated by additive scheme from ΔH_f^0

values for H_2NCHO (or $H_2NCH=CH_2$), H_2NMe and Me_2NH molecules [31]. The enthalpies of formation for HCOX (X = F-I) were calculated by additive scheme from known ΔH_f^0 values of their homologues CH_3COX molecules ([31] and Table 4). For example, $\Delta H_f^0[HCOF] = \Delta H_f^0[HCOOH](-90.5) + \Delta H_f^0[CH_3COF]$ (-105.7) - $\Delta H_f^0[CH_3COOH](-103.44) \approx$ -93 kcal mol^{-1}. Similarly, $\Delta H_f^0[OCH\text{-}O\text{-}CHO] = \Delta H_f^0[CH_3CO\text{-}O\text{-}COCH_3](-136.83) - 2\Delta H_f^0(CH_3COOCH_3)(-98.45) + 2\Delta H_f^0(HCOOCH_3)(-85.0) \approx -110$ kcal mol^{-1}. ΔH_f^0 values for $HC{\equiv}CCH=O$ (24.5) and $HC{\equiv}CCH=CH_2$ (69.8) are taken from Ref.3. The heats of formation for $ClC{\equiv}CCHO$ and $BrC{\equiv}CCHO$ molecules (Table 1) were estimated by additive scheme using ΔH_f^0 values for $ClC{\equiv}CH$ (45.5), $BrC{\equiv}CH$ (58) and $HC{\equiv}CCHO$ (24.5) [3]. Since what kind of Hal/CHO interaction (repulsive, attractive or zero) might appear in disubstituted acetylene is unknown (for details see Ref.3) we just applied the additive scheme without introducing any correction term.

$\Delta H_f^0(CH_3COCN)$ was estimated by macroincremental scheme [20]: $\Delta H_f^0[CH_3COCN] = \Delta H_f^0[CH_3COCF_3](-200.7)$[20,33] - $\Delta H_f^0[CH_3CF_3]$(-179.5[4]) + $\Delta H_f^0[CH_3CN$(18[4]) = -3.2 ≈ -3 kcal mol^{-1}. The CH_3COCF_3 molecule was selected as a model compound due to close EN values for CF_3 (7.7) and NC-groups (7.9) [3]. Probably, because of expected larger steric CO/CF_3 interaction compared with that for CO/CN pair ΔH_f^0 CH_3COCN might appear to be even more negative. The literature experimental value is 6.2±6.2 kcal mol^{-1} [34]. The enthalpy of formation for $Me_2C=CHCHO$ molecule was calculated using additive (macroincremental) scheme introducing the small correction term SE: $\Delta H_f^0[Me_2C=CHCHO] = \Delta H_f^0[CH_2=CHCHO](-16.5) + \Delta H_f^0[Me_2C=CH_2](-4.0) - \Delta H_f^0[CH_2=CH_2](12.55)$ – SE(~2) = -35.05 ≈ 35.0 kcal mol^{-1}. The stabilizing energy SE = 2 kcal mol^{-1} appeared due to polar interaction of electron donating Me- and electron withdrawing CHO-groups with EN 4.8 and 7.2 units, respectively [3]. For example, if $CH_2=CH_2 \rightarrow MeCH=CH_2$ replacement gives $\Delta\Delta H_f^0$ –7.77 kcal mol^{-1} [31] such replacement in $CH_2=CHCHO \rightarrow$ *Z*-$MeCH=CHCHO$ or $CH_2=CHCOOH \rightarrow$ *E*- $MeCH=CHCOOH$ gives SE –1.71 or –1.96 kcal mol^{-1}, respectively. Additive (macroincremental) scheme was applied for estimation of $\Delta H_f^0[Cl_2C=CClCH=CH_2] = \Delta H_f^0[H_2C=CHCH=CH_2](26.29) + \Delta H_f^0[Cl_2C=CHCl]$(-2.3[16]) - $\Delta H_f^0[CH_2=CH_2](12.55) = 11.44 \approx 11.5$ kcal mol^{-1}.

For calculation of ΔH_f^0 CCl_3CHO molecule we first estimated ΔH_f^0 CCl_3COOH. Using ΔH_f^0 CCl_3COCl (-57.3[31]) and CCl_3COOPr (-109.9) and Benson's contributions [36] we derived ΔH_f^0 CCl_3COOH –102.71 and –101.79 kcal mol^{-1}, respectively. Taking the mean value –102.25 and using again Benson's group contributions [36] we estimated $C(Cl)_3(CO)$ group contribution –9.05 kcal mol^{-1} and then calculated $\Delta H_f^0[CCl_3CHO] = [C(Cl)_3(CO)] + [C(H)(CO)R]$ = -9.05 – 29.0[36] = -38.15 ≈ -38.1 kcal mol^{-1}. Now we have $\Delta\Delta H_f^0\{[C(Cl)_3(C)$(-19.62[36]) $\rightarrow [C(Cl)_3(CO)(-9.05)]\}$ = 10.57 kcal mol^{-1}. Since the Br-atom is larger then Cl-atom we ascribe arbitrary larger $\Delta\Delta H_f^0\{[C(Br)_3(C)$(15.84)[36] $\rightarrow [C(Br)_3(CO)]\}$~ 12 kcal mol^{-1}. Thus, $[C(Br)_3(CO)] \approx 15.84 + 12 \approx 28$ kcal mol^{-1} and $\Delta H_f^0[CBr_3CHO] = 28 - 29.1 \approx -1$ kcal mol^{-1}.

The ΔH_f^0 values for some of $XCH=CH_2$ molecules were calculated applying enthalpic shift procedure originally suggested by Benson [37] then in Ref. 20 and in many other works (see Ref. 3) and introduced in practice as a completed methodology in Ref. 3. As a model system for $XCH=CH_2$ molecules the substituted benzenes PhX were selected with now well known enthalpic shift $\Delta\Delta H_f^0(CH_2=CHX \rightarrow PhX) \approx 7.2$ kcal mol^{-1} [3, 20, 38-40]. Thus, taking ΔH_f^0 –24.67 [31] for PhCOCl, -20.72 [31] for $PhCOCH_3$, -17.27 [32, 41] for $PhOCH_3$ and adding ~ -7.2 kcal mol^{-1} we obtained ΔH_f^0 values –32, -28.5 and –24.5 kcal mol^{-1} for $CH_2=CHCOCl$, $CH_2=CHCOCH_3$ and $CH_2=CHOCH_3$

molecules, respectively. A larger procedure was performed for calculation of the enthalpies of formation for $CH_2{=}CHEH_2$ (E = As, Sb and Bi) molecules. The ΔH_f^0 values for model $PhEH_2$ molecules are derived by interpolation of the data for EH_3 and EPh_3 molecules [interpolated $\Delta\Delta H_f^0$ and ΔH_f^0 values in kcal mol^{-1} – in square brackets]

$$\begin{array}{lccccccc} & \mathrm{AsH_3} & \xrightarrow{[+27]} & \mathrm{PhAsH_2} & \xrightarrow{[+27]} & \mathrm{Ph_2AsH} & \xrightarrow{[+27.5]} & \mathrm{Ph_3As} \\ \Delta H_f^0 & 15.9\ [42] & & [43] & & [70] & & 97.5\ [43] \\ & \mathrm{SbH_3} & \xrightarrow{[+29.8]} & \mathrm{PhSbH_2} & \longrightarrow & \mathrm{Ph_2SbH} & \longrightarrow & \mathrm{Ph_3Sb} \\ \Delta H_f^0 & 34.7\ [42] & & [64.5] & & [94.5] & & 124\pm 3.8\ [4 \\ & \mathrm{BiH_3} & \xrightarrow{[+30.5]} & \mathrm{PhBiH_2} & \xrightarrow{[+30.5]} & \mathrm{Ph_2BiH} & \xrightarrow{[+30.5]} & \mathrm{Ph_3Bi} \\ \Delta H_f^0 & 54\ [42] & & [82.5] & & [113] & & 143.5\ [44] \end{array}$$

Now, taking ΔH_f^0 (calc.) for $PhAsH_2$, $PhSbH_2$ and $PhBiH_2$ we add ~ - (7.2-7.5) kcal mol^{-1} [3,20] and obtain ΔH_f^0 values for $CH_2{=}CHAsH_2$, $CH_2{=}CHSbH_2$ and $CH_2{=}CHBiH_2$ molecules 35.5, 57 and 75 kcal mol^{-1}. Earlier ΔH_f^0 $CH_2{=}CHPH_2$ 19 kcal mol^{-1} was estimated by other methods [32]. We leave this value for calculation of $CH_2{=}C(\bullet)PH_2$ free radical although estimation of $CH_2{=}CHPH_2$ from ΔH_f^0 Ph_3P gives close results (ΔH_f^0 and $\Delta\Delta H_f^0$ – in kcal mol^{-1}):

$$\begin{array}{lccccccc} & \mathrm{PH_3} & \xrightarrow{[+25.2]} & \mathrm{PhPH_2} & \xrightarrow{[+24]} & \mathrm{Ph_2PH} & \xrightarrow{[+24.5]} & \mathrm{Ph_3P} \\ \Delta H_f^0: & 1.3\ [42] & & [26.5] & & [50.5] & & [75] \end{array}$$

The ΔH_f^0 of Ph_3P is rather uncertain. Several values are quoted: 71.9±3.8 [44], 76.5 [45], 78±5 [46] and 78.4±5 [43] kcal mol^{-1}. We suggest the value 75 kcal mol^{-1} as the compromise value. Now, we calculate $\Delta H_f^0\{CH_2{=}CHPH_2] = 26.5 - 7.2 = 19.3$, compare with 19 kcal mol^{-1} [32]. From Q values for $CH_2{=}CH\bullet + CH_2{=}CHEH_2 + CH_2{=}C(\bullet)EH_2 + Q$ isodesmic reactions (E = N, As, and Sb) (Table 3) we by – inter- and extrapolation estimate those Q values for E = P and Bi:

EH_2 :	H_2N	PH_2	AsH_2	SbH_2	BiH_2
Q (kcal mol^{-1}):	4.76	[7]	9.2	10	[11]

then calculate the enthalpies of formation for $CH_2{=}C(\bullet)PH_2$ and $CH_2{=}C(\bullet)BiH_2$ free radicals, e.g. $\Delta H_f^0\ [CH_2{=}C(\bullet)PH_2] = \Delta H_f^0\ [CH_2{=}CH\bullet] - \Delta H_f^0\ [CH_2{=}CH_2] + \Delta H_f^0\ (CH_2{=}CHPH_2) - Q = 70 - 12.55 + 19.3 - 7 = 70$ kcal mol^{-1} and $\nu_{CH}\ [CH_2{=}C\underline{H}PH_2] = \nu_{CH}\ (CH_2{=}CH_2)(3060) - Q\ (7) \times 11$ (11 cm^{-1} – equivalent for 1 kcal mol^{-1} for vinylic =C-H bond) = ~ 2980 cm^{-1}.

For estimation of ΔH_f^0 $CH_2{=}C(X)Me$ molecules for two of them (X = Me and Cl) we possess experimental values, i.e. –4.0 (Me) and –5.0±2.2 (Cl) kcal mol^{-1} [31] the latter having rather large uncertainty. From these data we gain $\Delta\Delta H_f^0\ [CH_2{=}CHMe(4.88) \rightarrow CH_2{=}CMe_2\ (-4.0)] = -8.88$ and $\Delta\Delta H_f^0\ \{CH_2{=}CHCl\ (-5.2) \rightarrow CH_2{=}C(Cl)Me\ (-5)] = -10.2$ kcal mol^{-1}. The latter value seems quite reasonable since the observed difference –10.2 – (-8.8) = -1.4 kcal mol^{-1} (revealing stabilization of system due to CH_3/Cl polar effect) might be smaller compared with 1,2-isomers (see above). Taking the known EN values for X-substituents 10 (F), 9.0 (OH), 7.9 (CN), 7.4 (MeO), 7.1 (Cl), 6.2 (Br), 5.3 (I), 4.8

(Me) [3] and $\Delta\Delta H_f^0$ values –8.88 [$CH_2{=}CHMe \rightarrow CH_2{=}C(Me)_2$] and –10.2 [$CH_2{=}CHCl \rightarrow CH_2{=}C(Me)Cl$] kcal mol^{-1} we roughly assign the following $\Delta\Delta H_f^0$ [$CH_2{=}CHX \rightarrow CH_2{=}C(Me)X$] values –11.5 (F), -11 (OH), -11(CN), -10.5(MeO), -10.2 (Cl), -9.7 (Br), -9.2 (I) and using the ΔH_f^0 values for $CH_2{=}CHX$ obtain the following ΔH_f^0(calc.) for $CH_2{=}C(X)Me$ molecules: -46.5 (X = F), -41.4 (OH), 32 (CN), -35 (MeO), -5.0 (Cl) [31], 8.3 (Br), 22.8 (I). According to Ref.20 such substituents as OH, OMe, CN, Cl and Me have similar steric requirements while Br and I are larger in their "size" compared with Me-group in $CH_2{=}CMe_2$ molecule. Therefore, we slightly increase their ΔH_f^0 values to 8.5 and 23.5 kcal mol^{-1}, respectively.

Recently, the ΔH_f^0 –65.26 kcal mol^{-1} for •$CH_2C(F){=}O$ free radical was estimated [47] (compare with our value –59 or –60.5 [30] kcal mol^{-1}). When this one is inserted in isodesmic reaction •CH_2CHO (3) + $CH_3C(F){=}O$ (-105.66) → •$CH_2C(F){=}O$ (-65.26 [47]) + CH_3CHO (-39.73 kcal mol^{-1}) + Q the positive Q value +2.33 kcal mol^{-1} is obtained revealing the stabilization (?) of the free radical center at H-replacement by electron-withdrawing F-atom in non-conjugative position. This is doubtful result.

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