Determination of enthalpies of formation of organic free radicals from bond dissociation energies
3.* Cyclic and conjugated hydrocarbon radicals

Yu. D. Orlov[a] and *Yu. A. Lebedev[b]*

[a]*Tver' State University,*
33 ul. Zhelyabova, 170000 Tver', Russian Federation.
Fax: +7 (082 2) 33 1274
[b]*Institute of Chemistry of Non-Aqueous Solutions, Russian Academy of Sciences,*
1 ul. Akademicheskaya, 153045 Ivanovo, Russian Federation.
Fax: +7 (093 2) 37 8511

The values of C—H and C—I bond dissociation energies were used to calculate the enthalpies of formation (ΔH_f°) of 20 cyclic and conjugated hydrocarbon radicals (R·). The values of ΔH_f°(R·) were analyzed in terms of the quantitative structure—property correlation based on the additive-group model, and the reliability of these data was shown. Based on the correlation, several strain energies of cycles and energies of conjugation of a lone electron with a π-system were calculated. The additive-group method for calculation of ΔH_f° can be extended for radicals of the naphthalyl type.

Key word: hydrocarbon radicals, enthalpies of formation, structure—property correlation, calculation methods, strain energies of cycles, conjugated energies of a lone electron.

The results of studies on the thermochemistry of organic free radicals (R·) have been described previously.[1—5] The studies were directed to the extension of the data bases of enthalpies of formation (ΔH_f°) of R·, refinement of the known ΔH_f°(R·) values, and investigation of the structure—property correlation for new classes of R·.

In this report, we present the results of determination of ΔH_f°(R·) values from the published values of dissociation energies of chemical bonds (D). The following equation was used for the calculation of the ΔH_f°(R·) values:

$$D(R_1—R_2) = \Delta H_f^\circ(R_1\cdot) + \Delta H_f^\circ(R_2\cdot) - \Delta H_f^\circ(R_1R_2), \quad (1)$$

where $D(R_1—R_2)$ is the dissociation energy of the $R_1—R_2$ bond in the starting molecule R_1R_2, and ΔH_f° are the enthalpies of formation of the $R_1\cdot$ and $R_2\cdot$ radicals and the starting R_1R_2 molecule.

As a result, ΔH_f° of the following cyclic and conjugated radicals were determined: octen-1-yl-3 (1), octen-2-yl-4 (2), 4-methylpenten-2-yl-4 (3), pentadien-2,3-yl-5 (4), cyclohepten-2-yl-1 (5), cyclooacten-2-yl-1 (6), bicyclo[2.2.1]heptyl-1 (norbornyl-1) (7), bicyclo[2.2.2]-octyl-1 (8), 1-phenylcyclopentyl (9), 1-phenylcyclohexyl (10), indanyl-1 (11), tetralinyl-1 (12), 1-methyltetralinyl-1 (13), 1,2-dimethyltetralinyl (14), naphthalenyl-1 (15), naphthalenyl-2 (16), 1-naphthalenyl-1-ethyl-1 (17), acenaphthenyl-1 (18), 3,4,5-trihydroacenaphthenyl-1 (19), and 9,10-dihydrophenanthrenyl-9 (20).

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* For Part 2, see Ref. 1.

The ΔH_f°(R·) values found, reference $D(R—X)$ values, and auxiliary ΔH_f°(RX) values are presented in Table 1, which also includes the corresponding literature sources. Some ΔH_f°(RX) values were calculated from the additive-group method with parametrization.[11]

The ΔH_f°(RI) values for R· = 7 and 8 were determined by the method of substitution increments, according to which

$$\Delta H_f^\circ(\text{RI}) = \Delta H_f^\circ(\text{RH}) + I(\text{H} \to \text{I}), \quad (2)$$

where $I(\text{H} \to \text{I})$ is the increment of substitution of H by I. The ΔH_f°(RH) values[10] equal to (-54.9 ± 4.7) kJ mol^{-1} for R· = 7 and (-99.0 ± 1.1) kJ mol^{-1} for R· = 8 were used. In this case, the substitution increment $I(\text{H} \to \text{I})$ is equal to the difference between the contributions of the CI and CH groups to ΔH_f°, which, according to the data published previously,[11] is $53.6 - (-10.0) = 63.6$ kJ mol^{-1}.

The ΔH_f°(RH) value for R· = 9 was calculated by Scheme (3) of the method of macroincrement thermochemical modeling ΔH_f°(RH)/kJ mol^{-1}

| (31.8) | -16.7 ± 1.5 | -106.2 ± 0.8 | -154.7 ± 1.0 | (3) |
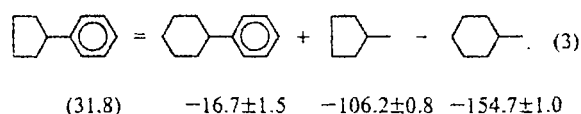
The calculated ΔH_f° value close to that found from the parameters of the additive-group scheme[11] (33.7 kJ mol^{-1}) is presented in parentheses hereinafter; the ΔH_f° values

are taken, except for the specially mentioned cases, from the reference book.[10] Scheme (3) also takes into account the conformational effect of the molecule on its ΔH_f° and, hence, it was preferred.
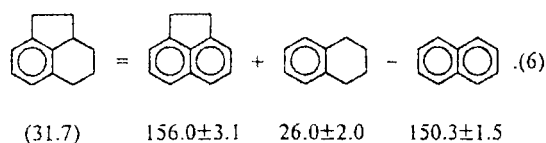
The enthalpies of formation (ΔH_f°/kJ mol^{-1}) of methyl-substituted tetralines (R = 13 and 14) were calculated from Schemes (4) and (5).

$$(0.8) \qquad 26.0\pm2 \qquad -179.9\pm1.9 \quad -154.7\pm1.0$$
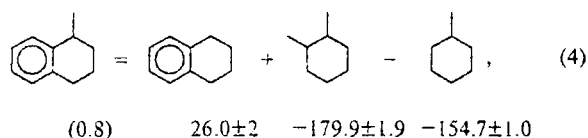
The ΔH_f°/kJ mol^{-1} value for 1-methyltetraline calculated by Scheme (4) was used in Scheme (5).

$$(24.4) \qquad 0.8 \qquad -179.9\pm1.9 \quad -154.7\pm1.0$$
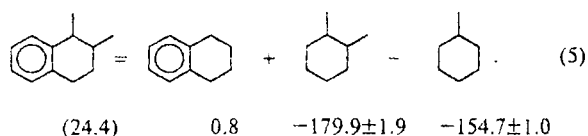
The ΔH_f°(RH)/kJ mol^{-1} value for R = 19 was calculated from the following scheme:

$$(31.7) \qquad 156.0\pm3.1 \quad 26.0\pm2.0 \quad 150.3\pm1.5$$

We determined the $\Delta H_f^\circ(R^\cdot)_{calc}$ values presented in Table 1 by the previously offered method[5-8] based on the additive-group model using the parameters presented previously.[6-8] It should be mentioned that the $\Delta H_f^\circ(R^\cdot)$ values found from the D and $\Delta H_f^\circ(R^\cdot)_{calc}$ values agree well. The difference between these values does not exceed 8 kJ mol^{-1}, which is comparable with an average error of reference $\Delta H_f^\circ(R^\cdot)$ values.

The values of conjugated energies (E_s) of a lone electron with a π-system of unsaturated alkyls were calculated from the known procedure,[8] which in several cases gives the same E_s for similar conjugations. According to this, for R = 1, 2, 3, 5, and 6, conjugation occurs *via* the allylic type, and $E_s = E_s(C=C-C^\cdot) = -52.0$ kJ mol^{-1}.[8] The benzyl-type conjugation takes place in radicals 9—16 and 19, and $E_s = E_s(Ph-C^\cdot) = -29.3$ kJ mol^{-1}.[8]

The values of strain energies of cycles (E_c) in cyclic radicals were calculated from the procedure[7,8] developed for monocyclic R$^\cdot$, including partially conjugated radicals. In this work, we found E_c for R = 5 and 6 using this procedure and, in several cases, used the values reported in Refs. 7 and 8. It is assumed that E_c for R = 9 and 10 are equal to E_c of the pentyl and hexyl radicals, respectively. The E_c value for indanyl-1 11 in the five-membered ring is equal to E_c of cyclopentenyl-3 (23.8 kJ mol^{-1}) (see Ref. 8). Similarly, the E_c values of radicals 12—14 presented in Table 1 are assumed to be equal to E_c of cyclohexenyl-3,[8] and that of radical 20 to E_c of cyclohexadien-1,3-yl-5.[8] The E_c values of radicals

Table 1. Thermodynamic data used for the calculation of $\Delta H_f^\circ(R^\cdot)$ (in kJ mol^{-1}) from $D(R-X)$ values in RX molecules

R$^\cdot$	X	$D(R-X)$	$\Delta H_f^\circ(RX)$	$\Delta H_f^\circ(R^\cdot)$	$\Delta H_f^\circ(R^\cdot)^a$	E_c^b	E_s^b
1	H	340.4[9]	−81.4±1.2[10]	41.0	37.3		−52.0
2	H	339.5[9]	−95.0[c]	26.5	26.4		−52.0
3	H	335.5[9]	−61.5±1.4[10]	56.0	50.1		−52.0
4	H	360.8[9]	133.1±0.8[10]	275.9			
5	H	339.7[9]	−9.2±1.1[10]	112.5	109.3	22.6	−52.0
6	H	342.3[9]	−27.0±1.2[10]	97.3	90.1	25.1	−52.0
7	I	236.6[12]	8.7[d]	138.5		99.7	
8	I	226.2[12]	−35.4[d]	84.0		67.0	
9	H	342.5[9]	31.8[d]	156.3	155.8	25.5	−29.3
10	H	349.6±1.2[13]	−16.7±1.5[10]	114.9	111.4	2.9	−29.3
11	H	352.5±0.7[9]	60.7±1.7[10]	194.5	194.0	23.8	−29.3
12	H	347.6±2.5[9]	26.0±2.0[10]	155.6	157.2	8.8	−29.3
13	H	331.9[9]	0.8[d]	114.7	122.6	8.8	−29.3
14	H	336.7[9]	24.4[d]	94.3	89.9	8.8	−29.3
15	I	273.4[12]	233.8±8.6	400.4			
16	I	274.8[12]	235.1±9.2	403.1			
17	H	357.6±5.0[13]	96.7[14]	236.3			
18	H	343.2[13]	156.0±3.1[10]	281.2			
19	H	329.8[9]	31.7[d]	143.5		27.4	−29.3
20	H	336.9±0.8[13]	159.7[15]	278.6		14.6	−45.6

[a] Calculated by the method and parametrization.[6-8]
[b] Calculated from the data in Refs. 6—8.
[c] Calculated from the additive-group method from the data in Ref. 11.
[d] Calculated in the present work.

7, **8**, and **19** and E_s(**20**), which cannot be calculated by the known procedure,[7,8] are also presented in Table 1. These valuues of E_c and E_s were calculated from the relation

$$E = \Delta H_f^\circ(\mathrm{R}^\cdot) - \Delta H_{hyp}(\mathrm{R}^\cdot), \qquad (7)$$

where $\Delta H_{hyp}(\mathrm{R}^\cdot)$ is the enthalpy of the hypothetical analog of the R$^\cdot$ radical considered, whose structure is similar in group composition to R$^\cdot$, but the cyclic strain (or conjugation of a lone electron) is absent. It was calculated as the sum of contributions of components of groups in R$^\cdot$. The corresponding parameters are presented in the literature.[6,8]

The data presented in Table 1 make it possible to perform further analysis of the structure—property correlation as applied to $\Delta H_f^\circ(\mathrm{R}^\cdot)$. For example, comparison of the ΔH_f°(**4**) value found and the ΔH_{hyp}(**4**) value calculated from the parameters described previously[6,8] results in the value E_s(**4**) > 0, which contradicts the physical sense of E_s. The contradiction can be eliminated by refining the contribution of the C_{dd}—$(C_d)_2$ group (C_d is the C atom forming the double bond) equal to 67.9 kJ mol^{-1} and estimated[8] from the ΔH_f° value of the $H_2C=C=C^\cdot Me$ radical ignoring a possible rearrangement of this radical to a radical of the π-type and conjugation of the lone π-electron.

Among the $\Delta H_f^\circ(\mathrm{R}^\cdot)$ values proposed, four values (R$^\cdot$ = **15**—**18**) are related to the series of radicals of the naphthalene class for which only one value ΔH_f°(1-C$^\cdot$H$_2$-naphthalyl = 252.7 kJ mol^{-1}) has been known previously.[16] Based on this value and new data for R$^\cdot$ = **15**—**18**, the contribution of the C_b—$(C_b)_3$ group (C_b is the "benzene" C atom) was estimated as 22.1 kJ mol^{-1}, and E_s in radicals of the 1-CH$_2$-naphthalyl type: E_s(1-C$_{10}$H$_7$—C$^\cdot$) as —43.7 kJ mol^{-1}. The ΔH_f° values (R$^\cdot$ = **15**—**18**) calculated from the indicated and other[6,8] parameters, as well as ΔH_f°(1-C$^\cdot$H$_2$C$_{10}$H$_7$)$_{calc}$ = 262.2 kJ mol^{-1}, agree satisfactorily with those found from the experimental data. This indicates further possibilities for the development of the procedure[5—8] suitable for calculating ΔH_f° of radicals with the complex structure, including aromatic polycycles.

This work resulted in the extension of the data bank on ΔH_f° of hydrocarbon radicals R$^\cdot$ by almost 20% to include ΔH_f° values for more than 120 radicals. The data proposed above can be used for estimating the values of heat effects for the processes involving radicals, D values of various bonds, and reference values that will be useful for comprehensive studies of the structure—property correlation in the thermochemistry of organic radicals and for the search for the relevant quantitative correlations.

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