Determination of enthalpies of formation of organic free radicals based on bond dissociation energies

4.[*] Alkyl-substituted derivatives of phenyl and benzyl

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The enthalpies of formation (ΔH_f°) of 16 alkyl-substituted phenyl and benzyl radicals ($R^\bullet$) were determined for the first time by the published values of energies of R—X bond dissociation. For the initial molecules of RX, alkyl-substituted benzenes, the additive-group procedure was developed for the calculation of ΔH_f°. In the framework of the additive-group model for considered $R^\bullet$, we studied the structure-property interrelation, analyzed the obtained $\Delta H_f^\circ(R^\bullet)$ values, and confirmed their reliability. The influence of nonvalent interactions on $\Delta H_f^\circ(R^\bullet)$ was systematized and detailed. The parameters, from which it is possible to calculate ΔH_f° of the 51 radicals, were proposed.

Key word: hydrocarbon radicals and molecules, enthalpies of formation, structure—property interrelation, calculation methods, intramolecular nonvalent interactions.

The thermochemical properties of aromatic radicals ($R^\bullet$) have first been generalized in Ref. 2, where the structure—property interrelation was studied in the framework of the additive-group approach for standard enthalpies of formation (ΔH_f°) of some $R^\bullet$. In this work, we present the results of ΔH_f° determination of alkyl-substituted derivatives of benzyl and phenyl on the basis of published data on dissociation energies (D) of R—X bonds in RX molecules, where R are hydrocarbon fragments (alkyl-substituted phenyls and benzyls), and X are univalent atoms (H or I). The presented work is a part of the systematic extension of the database of $\Delta H_f^\circ(R^\bullet)$, some results of this study have previously been described.[1,3–5]

The $\Delta H_f^\circ(R^\bullet)$ and D values are related by the following correlation:

$$D(R—X) = \Delta H_f^\circ(R^\bullet) + \Delta H_f^\circ(X) - \Delta H_f^\circ(RX), \qquad (1)$$

which also contains $\Delta H_f^\circ(RX)$, standard enthalpy of formation of the starting RX molecule. Based on correlation (1), we determined for the first time ΔH_f° of the following radicals: 2-methylphenyl (**1**), 2-ethylphenyl (**2**), 2,6-dimethylphenyl (**3**), 4-*tert*-butylbenzyl (**4**), pentamethylbenzyl (**5**), 1-(4-methylphenyl)eth-1-yl (**6**), 2-(2-methylphenyl)prop-2-yl (**7**), 2-(3-methylphenyl)prop-2-yl (**8**), 2-(4-methylphenyl)prop-2-yl (**9**), 2-(2,5-dimethylphenyl)prop-2-yl (**10**), 2-(4-isopropylphenyl)prop-2-yl (**11**), 2-(4-*tert*-butyl)prop-2-yl (**12**), 2-(2,5-dimethyl-4-isopropylphenyl)prop-2-yl (**13**), 1-(pentaethylphenyl)eth-1-yl (**14**), 1,2-diphenylethyl (**15**), and 2,4-dimethylbenzyl (**16**). We used the array of D(R—X) values presented in Table 1, which were ob-

Table 1. $\Delta H_f^\circ(R^\bullet)$ values determined by D(R—X) bond energies in RX molecules (kJ mol^{-1})

$R^\bullet$	X	D(R—X)	ΔH_f°(RX)	$\Delta H_f^\circ(R^\bullet)$
1	I	274.9 [6]	132.8±2.2 [9]	300.9
2	I	274.1 [6]	112.2 [a]	279.5
3	I	275.7 [6]	99.8 [b]	268.7
4	H	367.2 [7]	−56.0 [c]	93.2
5	H	364.1 [8]	−105.7 [10]	40.4
6	H	353.7 [8]	−3.2±1.3 [9]	132.5
7	H	356.0 [8]	−26.4 [c]	111.6
8	H	352.8 [8]	−29.0 [c]	105.8
9	H	347.7 [8]	−29.6 [c]	100.1
10	H	352.4 [8]	−60.3 [c]	74.1
11	H	338.5 [7]	−76.3 [c]	44.2
12	H	346.2 [8]	−102.6 [c]	25.6
13	H	359.9 [8]	−138.7 [c]	3.2
14	H	371.6 [8]	−224.3 [10]	−70.7
15	H	356.3 [8]	142.9±1.3 [9]	281.2
16	H	366.2 [8]	−13.8±1.0 [9]	134.4
17	H	368.0±2.2 [8]	19.1±1.1 [9]	169.1 [d], 166.5 [3]
18	H	370.9 [8]	17.3±0.8 [9]	170.2 [d], 166.5 [3]
19	H	362.9 [7]	18.0±1.0 [9]	162.9 [d], 166.5 [3]
20	H	367.5 [8]	15.9±1.3 [9]	133.6 [d], 133.0 [3]

[a] Calculation by Eq. (2).
[b] Calculation by Eq. (3).
[c] Calculation with the parameters presented in Table 2.
[d] Refined value.

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[*] For Part 3, see Ref. 1.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 6, pp. 923—929, June, 2001.

1066-5285/01/5006-963 $25.00

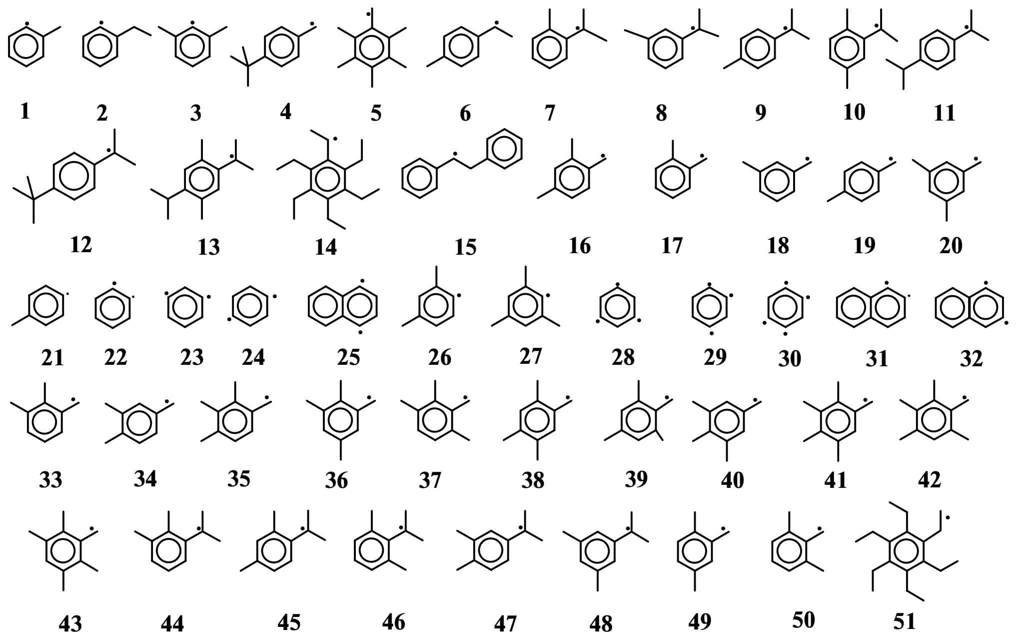


Fig. 1. Structural formulas and numeration of considered radicals.

tained[6—8] by the processing of the kinetic data on reactions of radical atom elimination in the framework of the models of intercepting parabolas[6] and intercepting Morse curves.[8] The structural formulas of the indicated and all other radicals considered in this work are presented in Fig. 1.

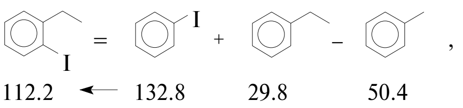
Only six experimental $\Delta H_f°(RX)$ values of molecules corresponding to radicals **1—16** are known of published data.[9,10] Thus, one of our main tasks was correct estimations of missing $\Delta H_f°(RX)$ values. Let us determine specific $\Delta H_f°(RX)$ and $\Delta H_f°(R^{\bullet})$ values by classes.

Determination of enthalpies of formation of molecules and radicals

The method of macroincrement thermochemical simulation (MTS) was used to determine unknown $\Delta H_f°(RX)$ values of two iodine-containing aromatic compounds (X = I, R = **2**, **3**).[11] Its essence is the simulation of the structure (property) of a compound on the basis of structures (properties) of simpler analogs (model compounds). With this purpose, a symbol "correlation" modeling the structure is composed. It is assumed that the value of the property for the simulated structure is calculated by a similar numerical correlation on the basis of the values of properties of model compounds. These values are usually written under the corresponding symbols in the symbol "correlation." This scheme clearly illustrates the performed calculation.

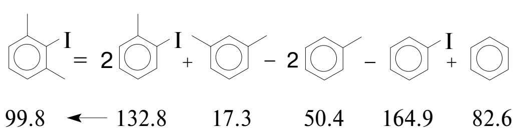
Using this procedure, we simulate the RI structures and calculate their $\Delta H_f°$ by the schemes presented below (figures under symbols are the $\Delta H_f°/\text{kJ mol}^{-1}$ values of the corresponding compounds)

for R = **2**



(2)

for R = **3**



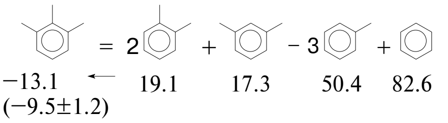
(3)

Using $\Delta H_f°(RI)$ calculated by Eqs. (2) and (3) and the experimental $\Delta H_f°(RI)$ value for R = **1**, we determined $\Delta H_f°$ of alkyl-substituted phenyls **1**, **2**, and **3** by correlation (1). All values used are presented in Table 1.

A wider series of $R^{\bullet}$ was considered for alkyl-substituted benzyls. For them the determination of $\Delta H_f°(RX)$ of the starting hydrocarbon molecules was unexpectedly a rather nontrivial problem. The corresponding experimental data are available only for 4 of 12 considered molecules. The use of the MTS method is impeded because the $\Delta H_f°$ values of model compounds are absent.

The additive-group approach[12,13] is distinguished of other methods for $\Delta H_f°$ calculation by the depth of quantitative data processing and wide covering of various classes of compounds. However, even in the last variant[13] this approach does not give satisfactory enthalpies of formation of alkyl-substituted benzenes. In fact, for hexamethylbenzene (Me_6C_6) the deviation of the calculated value from experiment is 11.1 kJ mol^{-1},[13] which exceeds by several times the error of the experimental determination of ΔH_f° of similar compounds.[9] Our analysis showed that this can be related to two factors: first, the nonadequate character of the model,[13] which ignores the interaction of substituents in positions 1,3 and 1,4 ($\Delta_{1,3}$ and $\Delta_{1,4}$), and, second, possible errors in reference data.

Thus, the reliable determination of desired ΔH_f°(RH) values requires the establishment of an adequate (in the framework of the determination error of ΔH_f°) quantitative structure—enthalpy correlation for alkyl-substituted benzenes. Let us consider the solution to this problem. At the first stage, we verified the database of reference ΔH_f° values by the MTS method (Eqs. (4)—(11)).



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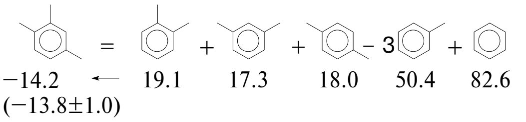

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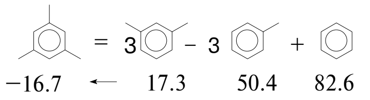

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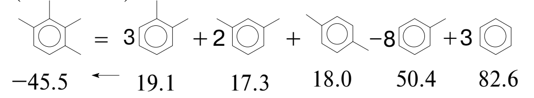

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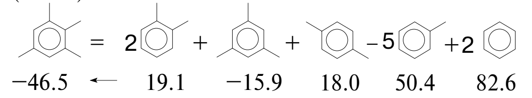

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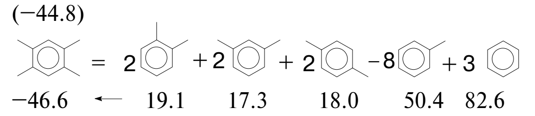

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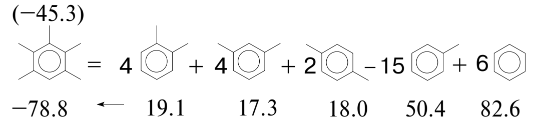

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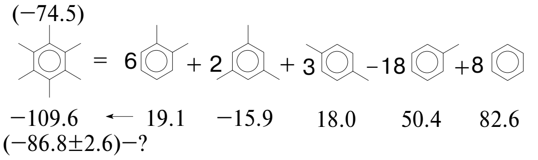


(11)

The published data on the ΔH_f° values of model and simulated compounds (for the latter the experimental values are presented in parentheses near the calculated values) were taken from the monographs.[9,10] A comparison of the calculated and experimental values shows a substantial divergence only for hexamethylbenzene (see Eq. (11)). If $\Delta H_f^\circ = -105.7$ kJ mol^{-1} [10] is taken as a reference, this divergence is eliminated. For other ΔH_f° values of simulated compounds (see Eqs. (4)—(10)) divergences are insignificant, and this allows us to consider $\Delta H_f^\circ(Me_6C_6) = -105.7$ kJ mol^{-1} [10] to be more adequate.

At the second stage, based on the selected database of ΔH_f° of methylbenzenes and published ΔH_f° values of other alkylbenzenes, we searched for the quantitative structure—property correlation for enthalpies of formation of these compounds in the gas phase in the framework of the additive-group approach. The increments to ΔH_f° of the interactions of alkyls $\Delta_{1,3}$ and $\Delta_{1,4}$ were considered. It should be emphasized that we accepted the energies of interaction of substituents in the benzene ring independent of the type of alkyl (Alk), which corresponds to the introduced designation $\Delta_{1,k}$(Alk—Alk) at k = 2—4. The parameters for the alkyl fragments and $C_B-(C_B)_2(H)$ were taken from the published work[13] (commonly accepted designations of groups are used[12,13]). The parameters were calculated by the special program, which accomplishes the least-squares method. Thus found increments of groups and interactions are presented in Table 2.

Table 3 contains ΔH_f° ($\Delta H_f^\circ{}_{calc}$) of gas-phase alkyl-substituted benzenes calculated with the indicated parameters and experimental data ($\Delta H_f^\circ{}_{exp}$). Note that the good agreement between these values was obtained for a wide class of compounds. Thus, in the framework of the additive-group approach we succeeded to deduce for the first time the quite adequate quantitative structure—property correlation for enthalpies of formation of gas-phase alkyl-substituted benzenes and propose a set

Table 2. Increments from groups and interactions to ΔH_f° of alkylbenzene molecules and radicals of phenyl and benzyl derivatives in the gas phase (kJ mol^{-1})

Group	Increment	Group	Increment
	Alkylbenzenes		
$C_B-(C_B)_2(H)$	13.77 [13]	$C-(C_B)(C)_3$	10.73
$C_B-(C_B)_2(C)$	23.34	$C-(C)_2(H)_2$	−20.90 [13]
$C-(C_B)(H)_3$	−41.84 [13]	$C-(C)_3(H)$	−10.00 [13]
$C-(C)(H)_3$	−41.84 [13]	$\Delta_{1,2}$(Alk—Alk)	2.11
$C-(C_B)(C)(H)_2$	−19.85	$\Delta_{1,3}$(Alk—Alk)	−0.50
$C-(C_B)(C)_2(H)$	−4.76	$\Delta_{1,4}$(Alk—Alk)	−1.12
	Phenyl and benzyl derivatives		
$C^\bullet{}_B-(C_B)_2$	260.9 [2,a]	$\Delta_{1,2}$(Alk—Alk)	2.11 [b]
$C^\bullet-(H)_2(C)$	148.49 [2,a]	$\Delta_{1,3}$(Alk—Alk)	−0.50 [b]
$C^\bullet-(H)(C)_2$	154.60 [2,a]	$\Delta_{1,4}$(Alk—Alk)	−1.12 [b]
$C^\bullet-(C)_3$	161.0 [2,a]	$\Delta_{1,2}(C_B{}^\bullet-Alk)$	8.6
$C_B-(H)(C_B)_2$	13.8 [2]	$\Delta_{1,3}(C_B{}^\bullet-Alk)$	— [c]
$C_B-(C)(C_B)_2$	16.6 [2]	$\Delta_{1,4}(C_B{}^\bullet-Alk)$	(4.9) [d]
$C-(H)_3(C)$	−41.04 [2,a]	$\Delta_{1,2}(C_B{}^\bullet-C_B{}^\bullet)$	(−131.0) [d]
$C-(H)_2(C)_2$	−21.76 [2,a]	$\Delta_{1,3}(C_B{}^\bullet-C_B{}^\bullet)$	(−67.0) [d]
$C-(H)(C)_3$	−13.39 [2,a]	$\Delta_{1,4}(C_B{}^\bullet-C_B{}^\bullet)$	−4.2
$C-(C)_4$	−1.61 [2,a]	$\Delta_{1,2}(C^\bullet-Alk)$	5.15
$C_B-(C_B)_3$	22.1 [3]	$\Delta_{1,3}(C^\bullet-Alk)$	4.36
$E_S(Ph-C^\bullet)$	−29.3 [2]	$\Delta_{1,4}(C^\bullet-Alk)$	3.56

[a] For the atom adjacent with the central atom of a given group, we assume $C\equiv C_B$.

[b] See alkylbenzenes.

[c] The increment was not estimated because experimental data are lacking.

[d] Estimated from one reference value.

Table 3. Enthalpies of formation (kJ mol^{-1}) of gas-phase alkylbenzenes

Compound	$\Delta H_f^\circ{}_{exp}{}^a$	$\Delta H_f^\circ{}_{calc}$	$\Delta\Delta H_f^{\circ b}$
C_6H_6 (**1**)	82.60	82.62	−0.02
MePh (**2**)	50.40	50.35	0.05
1,2-$Me_2C_6H_4$ (**3**)	19.10	20.19	−1.09
1,3-$Me_2C_6H_4$ (**4**)	17.30	17.58	−0.28
1,4-$Me_2C_6H_4$ (**5**)	18.00	16.96	1.04
1,2,3-$Me_3C_6H_3$ (**6**)	−9.50	−10.47	0.97
1,2,4-$Me_3C_6H_3$ (**7**)	−13.80	−13.20	−0.60
1,3,5-$Me_3C_6H_3$ (**8**)	−15.90	−15.69	−0.21
1,2,3,4-$Me_4C_6H_2$ (**9**)	−41.90	−42.25	0.35
1,2,3,5-$Me_4C_6H_2$ (**10**)	−44.80	−44.86	0.06
1,2,4,5-$Me_4C_6H_2$ (**11**)	−45.30	−45.48	0.18
Me_5C_6H (**12**)	−74.50	−74.53	0.03
Me_6C_6 (**13**)	−105.70	−104.70	−1.00
EtPh (**14**)	29.80	30.50	−0.70
1-Et—2-Me—C_6H_4 (**15**)	1.30	0.34	0.96
1-Et—3-Me—C_6H_4 (**16**)	−1.80	−2.27	0.47
1-Et—4-Me—C_6H_4 (**17**)	−3.20	−2.89	−0.31
PrPh (**18**)	7.90	9.60	−1.70
Pr^{i}Ph (**19**)	4.00	3.75	0.25
BuPh (**20**)	−13.10	−11.30	−1.80
Bu^{i}Ph (**21**)	−21.50	−21.34	−0.16
Bu^{s}Ph (**22**)	−17.40	−17.15	−0.25
Bu^{t}Ph (**23**)	−22.60	−22.60	0.00
1,2-Et_2—C_6H_4 (**24**)	−19.00	−19.51	0.51
1,3-Et_2—C_6H_4 (**25**)	−21.80	−22.12	0.32
1,4-Et_2—C_6H_4 (**26**)	−22.30	−22.74	0.44
1,2-Me_2—3-Et—C_6H_3 (**27**)	−29.70	−30.32	0.62
1,3-Me_2—2-Et—C_6H_3(**28**)	−29.70	−30.32	0.62
1,4-Me_2—2-Et—C_6H_3 (**29**)	−33.10	−33.55	0.45
1,2-Me_2—4-Et—C_6H_3 (**30**)	−33.10	−33.55	0.45
1,3-Me_2—4-Et—C_6H_3 (**31**)	−33.10	−33.55	0.45
1,3-Me_2—5-Et-C_6H_3(**32**)	−35.60	−35.54	−0.06
1-Pr—2-Me—C_6H_3 (**33**)	−21.60	−20.56	−1.04
1-Pr—3-Me—C_6H_4 (**34**)	−24.60	−23.17	−1.43
1-Pr—4-Me—C_6H_4 (**35**)	−25.00	−23.79	−1.21
1,2,3-Et_3—C_6H_3 (**36**)	−68.00	−70.02	2.02
1,2,4-Et_3—C_6H_3 (**37**)	−71.10	−73.25	2.15
1,3,5-Et_3—C_6H_3 (**38**)	−74.70	−75.24	0.54
1,2,3,4-Et_4—C_6H_2 (**39**)	−123.30	−121.65	−1.65
1,2,3,5-Et_4—C_6H_2 (**40**)	−122.80	−124.26	1.46
1,2,4,5-Et_4—C_6H_2 (**41**)	−123.30	−124.88	1.58
Et_5C_6H (**42**)	−175.20	−173.78	−1.42
Et_6C_6 (**43**)	−224.30	−223.80	−0.50
n-C_5H_{11}—Ph (**44**)	−34.40	−32.20	−2.20
n-C_6H_{13}—Ph (**45**)	−55.00	−53.10	−1.90
n-C_7H_{15}—Ph (**46**)	−75.60	−74.00	−1.60
n-C_8H_{17}—Ph (**47**)	−96.20	−94.90	−1.30
n-C_9H_{19}—Ph (**48**)	−116.90	−115.80	−1.10
n-$C_{10}H_{21}$—Ph (**49**)	−137.50	−136.70	−0.80

[a] The $\Delta H_f^\circ{}_{exp}$ values for compounds **1—8** and **13—23** are presented by published data,[9] for **9—12** and **24—49** according to Ref. 10.

[b] $\Delta\Delta H_f^\circ = \Delta H_f^\circ{}_{exp} - \Delta H_f^\circ{}_{calc}$.

of parameters for the calculation of ΔH_f° of other compounds of the considered series.

The proposed approach was used for the determination of ΔH_f°(RH) of the corresponding radicals **4**, **7—13**, and the found values are presented in Table 1. We also refined (by new published D(R—H) values) ΔH_f° of 2-methylbenzyl (**17**), 3-methylbenzyl (**18**), 4-methylbenzyl (**19**), and 3,5-dimethylbenzyl (**20**) radicals; all corresponding values are presented in Table 1. Due to an uncertainty of errors for most reference values (D and ΔH_f°(RX)), it was impossible to reliably determine errors of the found $\Delta H_f^\circ(R^\bullet)$ values, in our opinion, they do not exceed 8—10 kJ mol^{-1}.

Structure—property regularities

The additive-group model of the structure—property interrelation (for the thermochemical properties of $R^\bullet$)[14—17] in the previously published work[2] was developed for organic radicals containing blocks of conjugated bonds, including those of the phenyl and benzyl type. The quantitative correlation and parametrization[2] describe satisfactorily the structure—enthalpy of formation interrelation for these radicals. At the same time, the available[2] database of experimental $\Delta H_f^\circ(R^\bullet)$ values is insufficient and did not allow the authors to consider the problems on the influence of nonvalent interactions of the free valence and substituting groups and substituents themselves in the benzene ring on $\Delta H_f^\circ(R^\bullet)$. The last problem, as shown above, was not either solved for molecules.

The extension of the database of $\Delta H_f^\circ(R^\bullet)_{exp}$ groups (from experimental data) performed in this work allows the consideration of the influence of these nonvalent interactions on $\Delta H_f^\circ(R^\bullet)_{exp}$. We carried out the corresponding study in the framework of the additive-group model,[2] according to which $\Delta H_f^\circ(R^\bullet)$ can be presented as the sum of the following increments:

$$\Delta H_f^\circ(R^\bullet) = B^\bullet + \Sigma A_i + \Sigma\Delta_{1,k} + E_s, \tag{12}$$

where $B^\bullet$ is the increment of the group containing the free valence, A_i are the increments of other groups composing $R^\bullet$, $\Delta_{1,k}$ are the increments of nonvalent interactions of substituents in the benzene ring, and E_s is the conjugation energy of the free valence with the π-electron system of the radical. For radicals of the phenyl type (σ-radicals), $E_s = 0$. In this case, as shown by the analysis of experimental ΔH_f° values of radicals **1—3** and 4-methylphenyl (**21**), the adequate description of changes in $\Delta H_f^\circ(R^\bullet)$ in the framework of the correlation,[2] formally requires to take into account increments of interactions of the type "free valence—substituting group," *i.e.*, $\Delta_{1,k}(C_B - Y)$, where k = 2, 3, and 4 (*ortho*-, *meta*-, and *para*-positions of substituents, respectively).

Based on four reference ΔH_f° values of radicals **1—3** and **21** (Table 4), we estimated the $\Delta_{1,k}(C_B{}^\bullet - Y)$ values at k = 2 and 4 and Y = Me and Et. For both substituents, the $\Delta_{1,2}$ values are close, which allows us to assume, at this stage, that they are independent of the type of alkyl substituent, *i.e.*, equal for all alkyls. The $\Delta_{1,4}(C_B{}^\bullet$—Alk) value is not optimized because it was

Table 4. Calculated and experimental $\Delta H_f°(R^•)$/kJ mol^{-1}

$R^•$	$\Delta H_f°(R^•)_{calc}$	$\Delta H_f°(R^•)_{exp}$[a]	δ
1	300.3	300.9	0.6
2	278.5	279.5	1.0
3	270.1	268.7	1.4
21	(296.6)[b]	296.6 [18]	0
26	266.4	—	—
27	236.8	—	—
22	(446.0)[b]	446.0±12.5 [19]	0
23	(510.0)[b]	510.0±13.0 [19]	0
24	572.8	576.5±12.1 [19]	3.7
25	543.4	539.7±5.8 [20]	3.7
28	623.1	—	—
29	621.9	—	—
30	666.8	—	—
31	516.6	—	—
32	580.6	—	—
17	—	169.1	—
18	—	170.2	—
19	—	162.9	—
6	—	132.5	—
4	86.5	93.2	6.7
33	140.0	—	—
16	136.5	134.4	2.1
49[c]	—	134.0 [3]	—
50[d]	—	130.0 [3]	—
34	138.4	—	—
20	—	133.6	—
35	107.0	—	—
36	104.6	—	—
37	105.4	—	—
38	103.8	—	—
39	102.6	—	—
40	106.2	—	—
41	73.6	—	—
42	71.8	—	—
43	72.0	—	—
5	—	40.4	—
7	102.2	111.6	9.4
7	116.2[e]	111.6	4.6
8	—	105.8	—
9	—	100.1	—
44	84.4[e]	—	—
45	80.9[e]	—	—
10	67.3	74.1	6.8
10	81.3[e]	74.1	7.2
46	96.5[e]	—	—
47	68.8	—	—
48	67.0	—	—
11	—	44.2	—
12	—	25.6	—
13	−20.1	3.2	23.3
13	−6.1[e]	3.2	9.3
14	−103.3	−70.7(?)[f]	32.6
51	−81.4	—	—
15	274.7	281.2	6.5

[a] The $\Delta H_f°(R^•)_{exp}$ values without references were determined in this work (see Table 1).

[b] Conventional calculation due to uniqueness of the reference $\Delta H_f°(R^•)_{exp}$ value in the estimation of the correlation parameter (see Table 4).

[c] 2,5-Dimethylbenzene (**49**).

[d] 2,6-Dimethylbenzene (**50**).

[e] With a correction to the steric interaction of 14.0 kJ mol^{-1} (see text).

[f] See comments in text.

determined from one $\Delta H_f°$(**21**) value. The used correlation parameters[2] and found increments of interactions are presented in Table 2. Note that we used the $\Delta_{1,3}$(Me—Me) increment to $\Delta H_f°$(**3**), which is the same as a similar increment to $\Delta H_f°$ of the molecules in the gas phase (see Table 3). Interactions of this type were not considered previously.

In this connection, it is of interest to consider interactions of the "free valence—free valence" type. The consideration can be performed on the basis of experimental data on $\Delta H_f°$ of the benzene-1,2-diyl (**22**), benzene-1,3-diyl (**23**), benzene-1,4-diyl (**24**), and naphthalene-1,4-diyl (**25**) biradicals presented in Table 4. The found $\Delta_{1,k}(C_B{}^•—C_B{}^•)$ values are presented in Table 2. It is of interest that, unlike increments of the $\Delta(C_B{}^•—\text{Alk})$ type, they are negative, *i.e.*, the corresponding interactions stabilize the system. This can indicate the different natures of interactions of the $(C_B{}^•—C_B{}^•)$ and $(C_B{}^•—\text{Alk})$ types. In this work, these interactions are introduced formally, their physical sense should be considered in a special study at the quantum-chemical level.

The parameters for calculations of $\Delta H_f°$ of radicals of the benzyl type are also presented in Table 2. Here (as in Ref. 2) we assumed that E_s is independent of the type and number of alkyl substituents both in the benzene ring and at the C atom bearing the free valence and amounts to $E_s(\text{Ph—C}^•)$ = −29.3 kJ mol^{-1}.[2] At this stage, we introduced two new important statements concerning nonvalent interactions. First, the interactions of alkyl groups containing no free valence at all or in the α-position relatively to the benzene ring were assumed, as for molecules (see above and Tables 2 and 3), to be independent of the type of alkyl, and their increments to $\Delta H_f°(R^•)$ considered equal to the increments of similar interactions to $\Delta H_f°$ of the molecules (see Table 3). Second, interactions of alkyl substituents with the free valence on the atom directly bound to the benzene ring (in the α-position) and other alkyl groups in the benzene ring were also assumed independent of the type of alkyl.

Thus, the model[2] is supplemented by six parameters: increments $\Delta_{1,k}$(Alk—Alk) and $\Delta_{1,k}(C_B{}^•—\text{Alk})$, where k = 2, 3, and 4, the first three of them being taken from the procedure of calculation of $\Delta H_f°$ of molecules. This model allows a detailed consideration of the influence of nonvalent interactions on $\Delta H_f°(R^•)$ with a minimum increase in the number of parameters. The increments of all groups and interactions necessary for calculations of $\Delta H_f°$ of phenyl mono- and polyradicals and benzyl radicals are presented in Table 2. It contains all increments: both determined in the present work and taken from other works.

Table 4 contains the $\Delta H_f°$ values of alkyl-substituted mono- and polyradicals of the phenyl type and benzyl type radicals calculated in the framework of the structure—enthalpy of formation correlation (with the parameters from Table 2). Along with the data for radicals indicated above, Table 4 also contains the predicted $\Delta H_f°(R^•)_{calc}$ values for radicals, which supplement the considered classes, namely, for 2,4-dimethylphenyl (**26**), 2,4,6-trimethylphenyl (**27**), benzene-1,3,5-triyl (**28**), benzene-1,2,4-triyl (**29**), benzene-1,2,4,5-tetrayl (**30**), naphthalene-1,2-diyl (**31**), naphthalene-1,3-diyl (**32**), 2,3-dimethylbenzyl (**33**), 3,4-dimethylbenzyl (**34**), 2,3,4- (**35**), 2,3,5- (**36**), 2,3,6- (**37**), 2,4,5-(**38**), 2,4,6- (**39**), 3,4,5-(**40**) trimethylbenzyls, 2,3,4,5- (**41**), 2,3,4,6- (**42**), 2,3,5,6-tetramethylbenzyls (**43**), and 2-(*p,q*-dimethylphenyl)prop-2-yls at *p,q* = 2,3- (**44**), 2,4- (**45**), 2,6- (**46**), 3,4- (**47**), 3,5- (**48**).

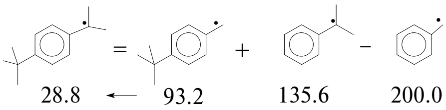
The $\Delta H_f°(R^•)_{calc}$ values calculated by the described method are compared in Table 4 with experimental $\Delta H_f°(R^•)_{exp}$ values proposed in this work or taken from literature. The comparison shows that, almost in all cases, deviations of these values $\Delta\Delta = -[\Delta H_f°(R^•)_{calc} - \Delta H_f°(R^•)_{exp}]$ range within a confidence interval for experimental $\Delta H_f°$ values of radicals of the considered classes, which is 8—10 kJ mol^{-1}. The maximum error of the calculated $\Delta H_f°$ values of radicals does not exceed this value.

Some results require additional comments. For example, much better agreement between the calculated and experimental data for radicals **7**, **10**, and **13** can be achieved when an additional correction to the *ortho*-interaction of the $C^•(Me)_2$ and Me groups equal to 14.0 kJ mol^{-1} is introduced. This correction seems physically justified for the following reason. The formation of the corresponding radical from the initial molecule (during the $Me_2C—H$ bond cleavage) changes the $sp^3 \rightarrow sp^2$ hybridization of the C atom that forms this bond. As a consequence, the conjugation of the unpaired π-electron with the π-system of the benzene ring system appears, the $C_B—C$ bond is shortened, two Me groups go to the ring plane, and additional steric hindrances appear in the planar $Me—C_B—C_B—C^•—Me$ group.

The δ deviation for radical **14** is too high. At the same time, the calculated $\Delta H_f°$ value for the 2-(pentaethylphenyl)ethyl radical (**51**) is very close to $\Delta H_f°(\mathbf{14})_{exp}$. Radicals **14** and **51** are formed from one initial Et_6C_6 molecule; **14** and **51** are formed when the H atom is eliminated from the α- and β-position, respectively, relatively to the benzene ring. Then the marked high δ value can be related to an inaccuracy in the indication of the radical center in the initial hydrogen elimination, *i.e.*, cleaved bond.[8]

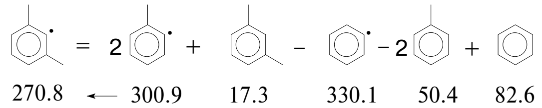
An uncertainty of the $\Delta_{1,3}(C_B{}^•—Alk)$ parameter (see Table 2) did not allow the prediction of $\Delta H_f°$ of alkyl-substituted phenyl of various degrees of substitution. In the prediction of $\Delta H_f°(R^•)$, we restricted our consideration by the calculation of the values for Me-substituted analogs of considered radicals. The described above method and presented set of parameters (see Table 2) allow the calculation of other Alk-substituted radicals of this type.

Presently, the described above MTS procedure becomes widely used for the determination of $\Delta H_f°$ of molecules. This procedure was not applied, most likely, for the calculations of $\Delta H_f°(R^•)$. The considered radicals are a good basis for the approbation of the MTS approach. The corresponding calculations were performed for seven radicals by Eqs. (13)—(19)



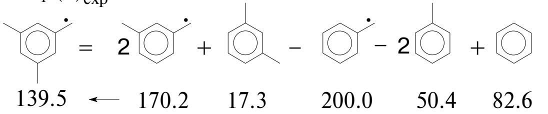
(13)

$\Delta H_f°(\mathbf{12})_{exp}$ = 25.6



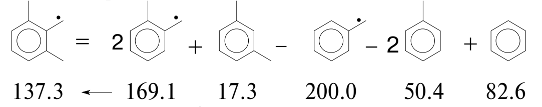
(14)

$\Delta H_f°(\mathbf{3})_{exp}$ = 268.7



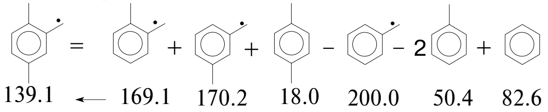
(15)

$\Delta H_f°(\mathbf{20})_{exp}$ = 133.6



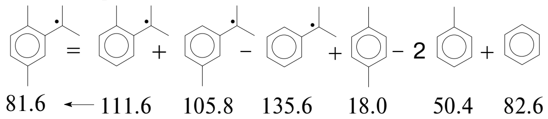
(16)

$\Delta H_f°(\mathbf{50})_{exp}$ = 130.0[8]



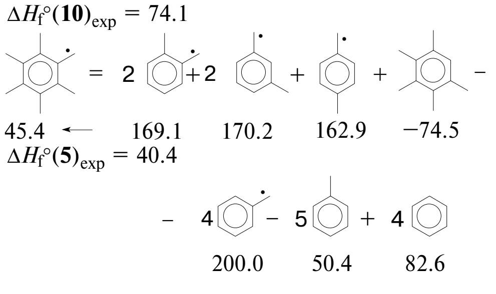
(17)

$\Delta H_f°(\mathbf{49})_{exp}$ = 134.0[3]



(18)

$\Delta H_f°(\mathbf{10})_{exp}$ = 74.1



$\Delta H_f°(\mathbf{5})_{exp}$ = 40.4

(19)

In the calculations we used the $\Delta H_f°$ values for molecules from the reference book,[9] and those for phenyl, benzyl, and 2-phenylprop-2-yl radicals are recommended in Ref. 5. The obtained results demonstrate clearly good possibilities and challenges of the MTS procedure applied to the prediction of $\Delta H_f°(R^\bullet)$.

In this work, we determined for the first time $\Delta H_f°$ for 16 and refined them for 4 alkyl-substituted phenyls and benzyls. This increased by more than 10% the number of available[21] data on the $\Delta H_f°$ values of hydrocarbon radicals. In addition, only several initial terms of homologous series were characterized by $\Delta H_f°$ in the previously considered classes of radicals. This consideration stimulated the detailed study of the structure—enthalpy of formation interrelation for the initial molecules, alkyl-substituted benzenes. As a result, the additive-group procedure for $\Delta H_f°$ calculation of these molecules was developed, which favored, to a greatest extent, the determination of the indicated above new $\Delta H_f°(R^\bullet)$ values.

Using the established $\Delta H_f°(R^\bullet)$ values, we studied the relation between the structure of $R^\bullet$ with their $\Delta H_f°$. In the framework of the additive-group model,[2] we systematized and analyzed in detail the influence of nonvalent interactions on $\Delta H_f°(R^\bullet)$. The parameters for forecast $\Delta H_f°$ calculations of 24 mono- and polyradicals were proposed. The possibilities and prospects of the use of the MTS procedure for $\Delta H_f°(R^\bullet)$ calculations were shown. These results deepen noticeably the quantitative and methodological basis of thermochemistry of organic free radicals.

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Received April 5, 2000;
in revised form December 8, 2000