Determination of enthalpies of formation of organic free radicals from bond dissociation energies

1. Hydrocarbon radicals

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The enthalpies of formation (ΔH_f°) for 24 hydrocarbon radicals ($R^\cdot$), mainly polycyclic aromatic radicals with the complex structure, were determined from the published data on bond dissociation energies. The ΔH_f° values of the corresponding molecules were calculated, in the majority of cases, by the macroincrement method. Calculations by the group contribution method were performed. Some $\Delta H_f^\circ(R^\cdot)$ values were compared to those calculated by the additive-group method. Calculations were performed, and the conjugation energies of the radicals were discussed. The errors of determination of the $\Delta H_f^\circ(R^\cdot)$ values found were estimated. Due to this work, the database for ΔH_f° values of hydrocarbon radicals was increased more than by 25%.

Key words: hydrocarbon radicals, thermochemical properties, calculation of properties.

Interest in the chemistry of free radicals ($R^\cdot$) is associated with their important role in processes of combustion, polymerization, pyrolysis, aging of polymeric materials, atmospheric changes, metabolism in living organisms, and others. Experimental studies of thermochemical properties of $R^\cdot$ are related to great methodological and technical difficulties due to the high chemical activity of $R^\cdot$.

Available databases and methods for calculation of thermochemical characteristics of organic free radicals are reviewed in Ref. 1. An automated databank on thermochemical properties of organic free radicals,[1,2] which collected in the systematized form all known values from reference books,[3,4] reviews,[5–6] and calculation-analytical works,[9,10] has been developed. This databank contains methods for calculation of thermochemical properties of organic radicals.[9,11–14] These methods were also used for analysis and systematization of the parameters.

The progress achieved during the past two decades is related to a considerable extent to the development of methods for experimental determination of enthalpies of formation $\Delta H_f^\circ(R^\cdot)$.

Many of these methods make it possible to determine the dissociation energy of chemical bonds $D(R_1—R_2)$ in molecules R_1R_2. The D values are related to $\Delta H_f^\circ(R^\cdot)$ and $\Delta H_f^\circ(R_1R_2)$ by the correlation

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

The absence of necessary values of ΔH_f° of molecules is a factor impeding calculations of new $\Delta H_f^\circ(R^\cdot)$ values.

In this work, we estimated ΔH_f° of hydrocarbon radicals **1**—**24**, which have been sufficiently well studied (the databank of $\Delta H_f^\circ(R^\cdot)$ up to 1987 [7] contains data for 80 these radicals, which is more than 25% of the overall number of the radicals in the databank). In addition, the ΔH_f° values previously known for some radicals were corrected in accordance with the results of new experimental studies.

The energies of abstraction of the H atom from the tertiary C atom in four methyl-substituted cycloalkanes have been determined[15] by the decarbonylation method based on comparative study of the reaction rates of decomposition and exchange. The ΔH_f° values of methylcyclohexane and methylcyclopentane in the gas phase are presented in the handbook.[16] For methylcyclobutane and methylcyclopropane, these values were calculated by the additive-group Benson method.[17] The D and ΔH_f° values, $\Delta H_f^\circ(R^\cdot)$ calculated from Eq. (1), and $\Delta H_f^\circ(R^\cdot)_{calc}$ obtained by the additive-group method for calculation of $\Delta H_f^\circ(R^\cdot)$ of alkyls and cycloalkyls are presented in Table 1.[11,14] The great divergence between these values for 1-methylcyclopropyl-1 **1** can be explained by the error in the experimental D value, which is indicated by the deviation of the obtained[15] $D(cyclo\text{-}C_3H_5—H)$ value (419.2 kJ mol^{-1}) from the commonly accepted[6] value of 444.7 kJ mol^{-1}. The $D(C—H)$

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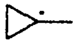
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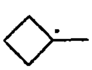
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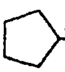
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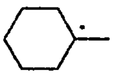
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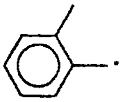
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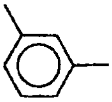
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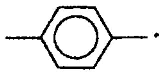
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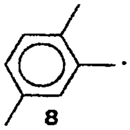
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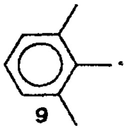
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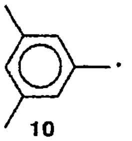
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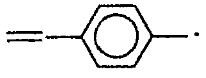
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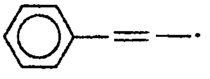
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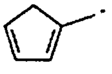
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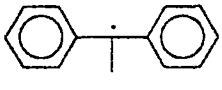
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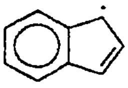
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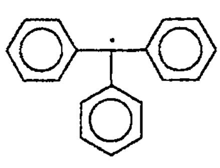
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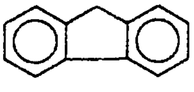
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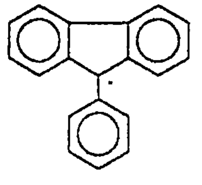
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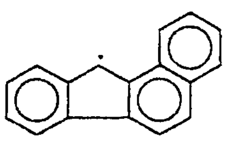
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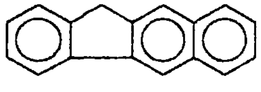
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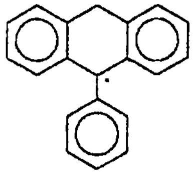
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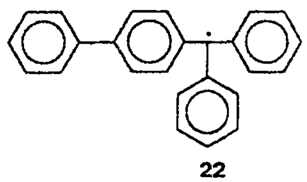
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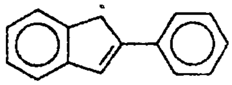
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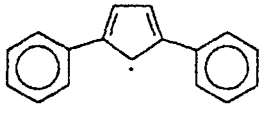
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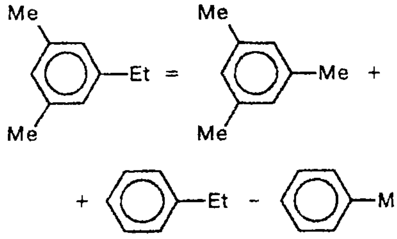
values determined previously[15] for cyclobutane, cyclopentane, and cyclohexane agree satisfactorily with the data of other works. Therefore, the $\Delta H_f°$ value obtained for 1-methylcyclopropane-1 is ambiguous. Three other $\Delta H_f°$ values of methylcycloalkyls **2—4** are sufficiently reliable. However, their errors, which are mainly due to errors of the experimental method,[15] is 8 kJ mol^{-1} according to our estimation. The next group of radicals studied includes methyl-substituted benzyls **5—10**. The *D* values of abstraction of the hydrogen atom of the methyl groups in *o*-, *m*-, and *p*-dimethylbenzenes have been determined by photoelectron spectroscopy.[18] The *D*(C—C) value for the symmetrical decomposition of di(*p*-methylphenyl)ethane, $(p\text{-MeC}_6H_4CH_2)_2$, has been also obtained[19] by studies of pyrolysis. The $\Delta H_f°$ values of molecules of dimethylbenzenes were taken from the reference book.[16] The $\Delta H_f°$ value of di(*p*-methylphenyl)ethane was obtained by the additive-group calculation from the published[17] parameters. Analyzing the $\Delta H_f°(R^\cdot)$ value (see Table 1), we can see that the $\Delta H_f°(p\text{-MeC}_6H_4CH_2)$ values obtained by different authors coincide.[18,19] The values obtained are reliable, which is additionally confirmed by their agreement with the calculated[9,11] values of $\Delta H_f°(R^\cdot)_{calc}$ (see Table 1). Unfortunately, it is still impossible to determine the effect of noncovalent interactions of methyl groups on $\Delta H_f°$ of methyl-substituted benzyls. As is known,[17] in similar molecules, these interactions give a contribution of 2.8 kJ mol^{-1} for *ortho*-substituted derivatives. However, this value is approximately twofold less than the error for the $\Delta H_f°(R^\cdot)$ values determined, which is most likely not less than 6 kJ mol^{-1}.

It has been previously mentioned[5] that the estimation of *D* values from data on radical thermal composition can lead to errors in the determination of activation energies E_a from the temperature dependence of the rate constant *k*(*T*). Reliable $\Delta H_f°(R^\cdot)$ values can often be obtained only by correction of the kinetic characteristics, E_a and *A* (pre-exponential factor).[5] Another method for determining $\Delta H_f°(R^\cdot)$ is acceptable and promising: from kinetic data, designing their correction and determining the necessity of this correction. This method can be applied in the case where data on thermal decomposition of a series of related compounds under similar conditions are available. It is also necessary to have reliable *D* (or E_a) values established independently for one or several compounds. The reliability of the *D* values suggested in the series can be determined by comparing with reference values; in the case of their divergence, the corresponding correction can be introduced. It is reasonable to assume that it is almost equal for all parameters of the series. Then, based on the corrected *D* values, we can obtain new $\Delta H_f°(R^\cdot)$ values by a standard method. We used[20] this method for the determination of $\Delta H_f°$ of methyl-substituted benzyls from the E_a value[20] for the thermal decomposition R—Me → R + Me. In this work,[20] we studied thermal decomposition of three methylethylbenzenes and three method. Three $D(RCH_2{-}Me)$ values were chosen as reference ones. They were calculated from the ΔH_f° values for methylbenzyls found in this work and from ΔH_f° for methylethylbenzyls determined previously.[16] The D values recalculated from E_a (see Ref. 20) are lower than the reference values, but the difference between them is approximately the same for all reference values and equal to 24 kJ mol^{-1}. The $D(RCH_2{-}Me)$ values corrected with account for this correction for dimethylethylbenzenes are presented in Table 1. Experimental ΔH_f° (gas) values for the corresponding molecules are lacking, and only their values for the liquid phase ΔH_f° (liq.) are available.[16] Then values of enthalpies of evaporation (ΔH_{vap}) for these molecules are necessary for determining ΔH_f° (gas). They were calculated from the following macroincrement scheme[27]



(2)

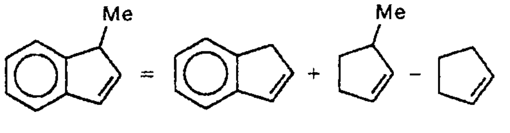
This correlation is also valid for ΔH_f° and ΔH_{vap} of the corresponding compounds. The ΔH_{vap} values calculated from Eq. (2) and two other similar correlations are equal to 52.3, 51.0, and 52.3 kJ mol^{-1}, respectively, for 2,5-, 2,6-, and 3,5-dimethylethylbenzenes. Auxiliary values of ΔH_{vap} used in correlations of type (2) were taken from the handbook.[28] The ΔH_f° (gas) values for three dimethylethylbenzenes are presented in Table 1. We preferred the calculation of ΔH_f° (gas) through ΔH_{vap} over the direct calculation of ΔH_f° (gas) from correlations (2), because the ΔH_{vap} value is less sensitive to modification of the chemical structure than ΔH_f° and, hence, gives a lower error. The values of ΔH_f° for three dimethylbenzyl radicals **8**—**10** are presented in Table 1. They are also compared with the values calculated by the method described.[9,11] Despite the good agreement of the values obtained with $\Delta H_f^\circ(R^\bullet)_{calc}$, the error for these values cannot be estimated due to the approximate character of the method, and they should be considered as estimates.

Table 1. Determination of $\Delta H_f^\circ(R^\bullet)$ through the $D(R{-}X)$ bond energies in RX molecules (kJ mol^{-1})

R	X	$D(R{-}X)$	$\Delta H_f^\circ(RX)$[a]	$\Delta H_f^\circ(R)$[b]	$\Delta H_f^\circ(R)$[c] (calc.)	$-E_s$
1	H[d]	398.7[15]	22.2	(202.9)[e]	246.3	0
2	H	394.5[15]	−2.5	174.0	180.2	0
3	H	382.4[15]	−106.2±0.8[16]	58.2	58.4	0
4	H	381.2[15]	−154.7±1.0[16]	8.5	14.1	0
5	H	365.3[18]	19.1+1.1[16]	166.5	166.5	29.3[f]
6	H	367.3[18]	17.3+0.8[16]	166.5	166.5	29.3[f]
7	H	366.5[18]	18.0+1.0[16]	166.5	166.5	29.3[f]
	=R[g]	255.5[19]	77.4	166.4	166.5	29.3[f]
8	Me	313[20][h]	−32.5	134	128.3	29.3[f]
9	Me	306[20][h]	−29.1	130	128.3	29.3[f]
10	Me	315[20][h]	−35.5	133	128.3	29.3[f]
11	Me	291.6[21][i]	95.1	239.9	—	59.8
12	Me	276.1[21][i]	95.4	224.7	—	80.6
13	H	361.9±8[23]	96.6	240.5	—	57.0
14	H	339±8[23]	124.4	245	256.0	46.1
15	Me	286.2[21][i]	136.9	276.2	—	61.8
	H	330.0[24]	163.4±2.1[16]	275.4	—	61.8
16	H[j]	338.1[24]	271.2±1.4[16]	391.3	—	26.5
	N_3	194.8[25]	606.7±2.5[25]	388	—	26.5
17	H	332.6[24]	187.4	302.0	—	52.2
18	H	310±4[26]	304.7	398	—	48.2
19	H	329.3[26]	249.5	360.8	—	—
20	H	328.0[26]	247.9	357.9		—
21	H	331[26]	277.0	390	—	26.2
22	H	339[37]	370.6	492	—	14.2
23	H	335±4[26]	262.2	379	—	46.9
24	H	314±4[26]	331.9	428	—	69.9

[a] The results of our calculations, which are described in detail in text, are presented without references. [b] Determined from Eq. (1). [c] Calculated by the additive-group method.[9,11] [d] $\Delta H_f^\circ(H^\bullet)$ = 218.0 kJ mol^{-1}.[4] [e] Doubtful values. For explanation, see text. [f] Determined previously.[9] [g] $\Delta H_f^\circ(Me^\bullet)$ = 146.8 kJ mol^{-1}. [i] Recalculated from E_a according to Ref. 22. [j] $\Delta H_f^\circ(N_3^\bullet)$ = 414 kJ mol^{-1}.

Unlike Ref. 20 considered above, it is not reasonable to use the correction method for the kinetic characteristics of radical thermal decomposition with abstraction of Me in five aromatic compounds studied previously,[21] because these compounds cannot be assigned to the same homologous series. Some of the kinetic characteristics[21] contain obvious contradictions. For example, the difference between log$A$ for the reactions of the $Ph_2CH{-}Me$ and $Ph_2C(Me){-}Me$ bond cleavage does not correspond to the known regularities of changes in log$A$ for hydrocarbons.[29] Therefore, we did not take into account the kinetic characteristics of these reactions. The $D(C{-}Me)$ value of the three remaining compounds obtained, as those described above, by the correlation[22] $D = E_a - RT_{av}$ (where T_{av} is the average temperature in the experiment) are presented in Table 1. The ΔH_f°/kJ mol^{-1} values of p-$CH_2{=}CHC_6H_4Et$ and $PhCH{=}CHEt$ were calculated by the additive-group method,[17] while for 1-methylindene, they were calculated by Eq. (3).



(3)

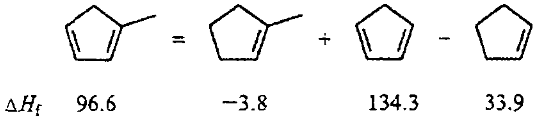
ΔH_f 136.9 163.4 7.4 33.9

Since this method for calculation of ΔH_f° of molecules will be repeatedly used in this work, let us accept that the auxiliary values of ΔH_f° (which are in the right part of the correlation) are chosen as in the handbook,[16] except the cases specially mentioned. The determined values of $\Delta H_f°$ for the molecules and radicals are presented in Table 1. For these radicals, the energies of conjugation stabilization E_s were calculated by the method described previously[9] (see Table 1). It is interesting that for *p*-vinylbenzyl **11**, the E_s value is almost twice as large as $E_s(PhCH_2) = -29.3$ kJ mol^{-1};[9] while for 3-phenylallyl **12**, E_s is close to E_s of dienyls (−78.7 kJ mol^{-1}).[9] $\Delta H_f°$ of inden-1-yl **15** will be discussed below.

Four values of *D*(C—H) in hydrocarbons are presented without $\Delta H_f°(R^{\bullet})$ values in Ref. 6 with citation of the previously published Ref. 23. Based on these values, we can determine $\Delta H_f°$ for two new radicals: 1,1-diphenylethyl **14** and 1-cyclopentadienylmethyl **13**. $\Delta H_f°$ (kJ mol^{-1}) of the corresponding molecules were calculated according to the following schemes.

$$Ph_2CHMe = Ph_2CH_2 + Me_3CH - Me_2CH_2 \qquad (4)$$

ΔH_f 124.4 153.9 −134.2 −104.7



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The $\Delta H_f°(Ph_2CH_2)$ value was taken from the handbook[30] (in the handbook[16] it is presented with a misprint). The additive-group method[17] gives a value of $\Delta H_f°$ for 1-methylcyclopentadiene that coincides with that calculated from Eq. (5). All values involved in the calculation of $\Delta H_f°(R^{\bullet})$ are presented in Table 1.

The determined value of $\Delta H_f°$ for 1,1-diphenylethyl **14** is confirmed by the calculation[9] and the fact that the E_s value obtained is close to E_s(diphenylmethyl) = −37.1 kJ mol^{-1}. According to our estimation, the error of determination of $\Delta H_f°(R^{\bullet})$ is equal to 9 kJ mol^{-1}.

The *D*(R—H) values in the gas and DMSO solution were compared for many molecules and different bonds.[24,26,31] In the majority of cases, the deviations of these values do not fall outside the scope of errors of their determination, and the deviations themselves are random. Therefore, it was concluded[24,26,31] that the *D*(R—H) values almost coincide in the gas and in DMSO solution. Accepting this statement and using the *D*(R—H) values, we determined $\Delta H_f°$ for several radicals. The values obtained were assigned to the ideal gas state and standard thermodynamic conditions. This is not quite rigorous, but justified in terms of the real error of *D*.

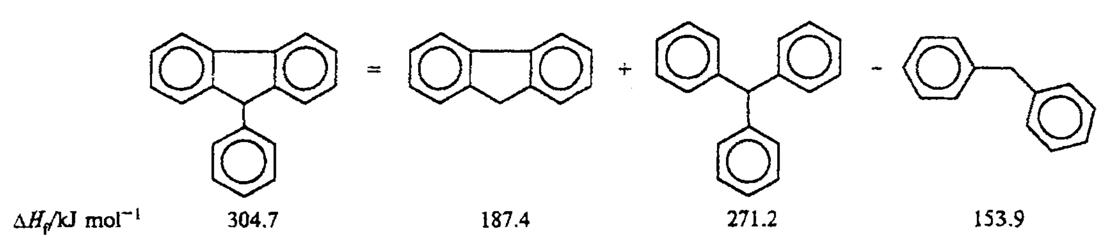
Using the published data,[24] we determined the $\Delta H_f°$ value of inden-1-yl **15** and corrected the $\Delta H_f°$ value of triphenylmethyl **16**. It should be noted that the $\Delta H_f°$ value of inden-1-yl **15** was estimated to be higher on the basis of the results of the kinetic studies.[21] Similarly, the $\Delta H_f°(Ph_3C^{\bullet})$ value can be determined from two sources. This allows comparison of the $\Delta H_f°(R^{\bullet})$ values obtained[24] in a solution of DMSO and from data of kinetic measurements. The *D*(C—H) values for indene and triphenylmethane, the $\Delta H_f°$ of these molecules, and the corresponding radicals are presented in Table 1. For inden-1-yl **15**, both values result in almost the same value of $\Delta H_f°$. The second value of $\Delta H_f°(Ph_3C^{\bullet})$ was recalculated on the basis of the data obtained and cited previously.[25] The $\Delta H_f°(Ph_3C^{\bullet})$ value determined[25] is equal to 328.9 kJ mol^{-1}, and it was also recommended in the handbook.[4] This value was obtained using $\Delta H_f°(N_3)$ = 439 kJ mol^{-1}.[32] The fact that the $\Delta H_f°$ values for the phenyl and benzyl radicals determined by a similar method contradict the commonly accepted values casts some doubt. The analysis showed that when the value $\Delta H_f°(N_3)$ = 414 kJ mol^{-1} recommended in the reference book[33] is chosen as the reference, the contradictions indicated are removed. For triphenylmethyl, we obtain $\Delta H_f°$ = 388 kJ mol^{-1}, which almost coincides with the estimation based on the published data.[24] The conjugation energies of the radicals considered were calculated from the method described previously.[9]

The enthalpies of formation of the other radicals presented in Table 1 were determined from the *D*(C—H) values obtained by the known method.[24] Experimental values of $\Delta H_f°$ of the starting molecules were not published, and the main difficulties were related to their determination. Let us present the corresponding consideration for each molecule.

Fluorene. Using $\Delta H_f°$ in the solid phase, $\Delta H_f°(s)$ = 88.2 kJ mol^{-1},[34] and the heat of sublimation, ΔH_s = 99.2 kJ mol^{-1},[28] we obtain $\Delta H_f°$ (gas) = 187.4 kJ mol^{-1}.

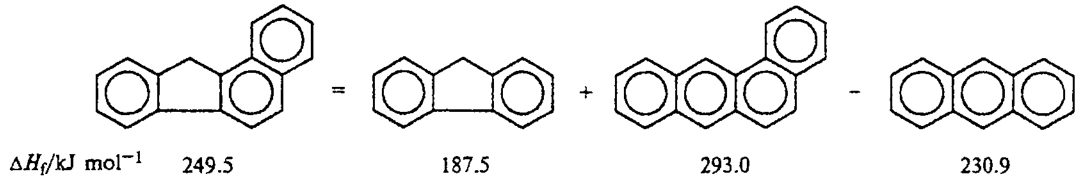
In other cases, we used the macroincrementing method, in terms of which the following schemes were simulated (Eqs. (6)—(12)).

9-Phenylfluorene



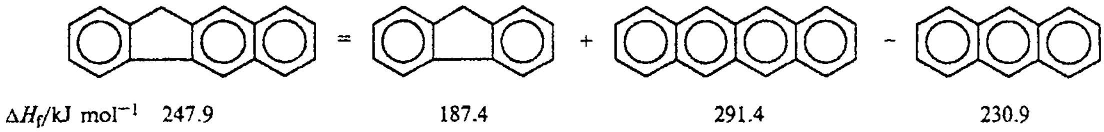
(6)

1,2-Benzofluorene



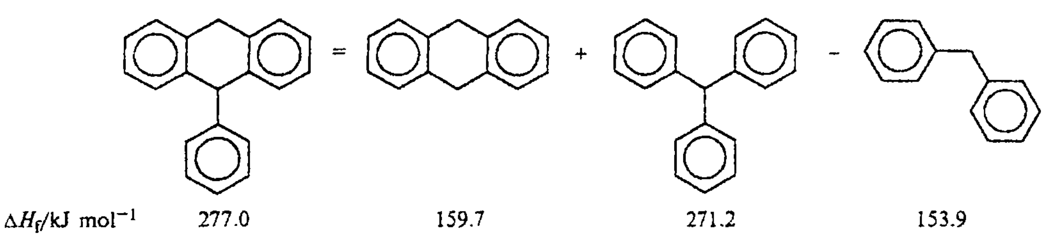
(7)

2,3-Benzofluorene



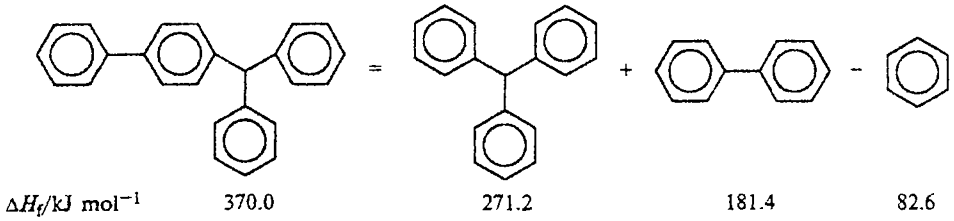
(8)

9-Phenyl-9,10-dihydroanthracene



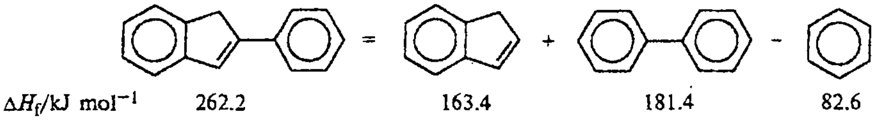
(9)

Diphenyl(*p*-biphenylyl)methane



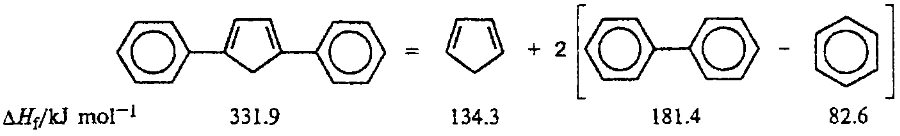
(10)

2-Phenylindene



(11)

1,4-Diphenylcyclopentadiene



(12)

Equations (11) and (12) do not quite adequately correspond to the molecules considered; however, they give not too rough estimations of their ΔH_f°. As mentioned above, the auxiliary values of ΔH_f° were taken from Ref. 16 (for the choice of the $\Delta H_f^\circ(Ph_2C^{\bullet}H_2)$, see above). In all cases except when especially mentioned, we consider the ΔH_f° values in the gas phase. The initial values of D(C—H) and the $\Delta H_f^\circ(R^{\bullet})$ values obtained are presented in Table 1 as well as the conjugation energies E_s calculated using the known procedure.[9] Correspondence with the general concepts of the structure theory is observed during their change depending on the structure. In fact, E_s for triphenylmethyl **16** and 9-phenyl-9,10-dihydroanthryl-9 (**21**) should be close. They differ from E_s of 9-phenylfluorenyl-9 (**18**) in which conjugation of two benzene rings results in a higher value of the stabilization energy of this radical and its similarity to that of fluorenyl-9 (**17**), which also corresponds to an approximate equality of the E_s values of the given radicals. A tendency of E_s to decrease is observed when phenyl substituents are introduced into the π-system of radicals. The errors of the seven latter values of $\Delta H_f°(R^·)$ in Table 1 are most likely somewhat higher than those for the other substances. This is related to an inevitable increase in the errors of calculation of $\Delta H_f°$ of molecules as they become more complex. In our opinion, the errors of the two latter $\Delta H_f°(R^·)$ values are maximum and not less than +14 kJ mol^{-1}. This is hardly better than +10 kJ mol^{-1} for the remaining five values.

Thus, in this work, we determined the $\Delta H_f°$ values for 24 hydrocarbon radicals. This extends the available databank of $\Delta H_f°$ of hydrocarbon radicals by more than 25%. Some of the values obtained are related to the terms of the well-studied series of radicals. $\Delta H_f°$ of polycyclic aromatic radicals, which have almost not been studied previously, are of considerably greater interest. This suggests that the values obtained can be used to develop a calculation method for the $\Delta H_f°$ of new classes of radicals.

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