

Enthalpies of formation of amidyl free radicals

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The enthalpies of formation (ΔH_f°) of twenty-one amidyl radical (R^\bullet) belonging to the formamidyl homological series were calculated using the published values of R—H bond dissociation energies. Among them, the ΔH_f° values of nine radicals were first calculated and those of eight radicals were refined. Most of the ΔH_f° values of corresponding starting molecules RH ($\Delta H_f^\circ(RH)$) were obtained using the macroincrementing schemes. Based on the group additivity scheme, the "structure—enthalpy of formation" relationships for the radicals considered were examined, the $\Delta H_f^\circ(R^\bullet)$ values were analyzed, and their reliability was confirmed. Parameters for calculating the ΔH_f° values of radicals belonging to this homologous series were suggested.

Key words: free radicals, polyfunctional formamidyl derivatives, organic molecules, enthalpies of formation, bond dissociation energies, phenomenological calculations, structure—property relationships.

Amides and their polyfunctional derivatives are widely used in technological processes of production of polymeric materials and pharmaceuticals. Here, an important role is played by free radicals. Therefore, determination and refinement of geometric parameters and the energy and thermodynamic characteristics of free radicals $R^1C(O)N^*R^2$ (R^1 , R^2 are univalent organic substituents) is topical.

Enthalpies of formation of radicals and molecules: a calculation procedure

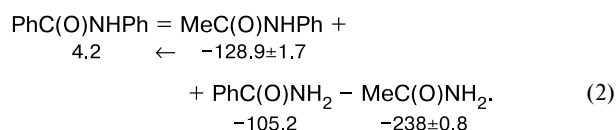
Information on the thermodynamic parameters of the radicals mentioned above is insufficient and experimental.¹ Original results were reported in Ref. 2. The thermodynamic parameters were calculated using the R—H bond dissociation energies ($D(R-H)$)³ and the main equation of thermochemistry of free radicals.

$$D(R-H) = \Delta H_f^\circ(R^\bullet) + \Delta H_f^\circ(H) - \Delta H_f^\circ(RH) \quad (1)$$

The data reported in Refs 1 and 2 did not include the published⁴ $D(R-H)$ values that allow one to increase the number of formamidyl derivatives characterized by the $\Delta H_f^\circ(R^\bullet)$ values

and to refine some of the known $\Delta H_f^\circ(R^\bullet)$ values² using the new data on $\Delta H_f^\circ(RH)$. The results of these calculations are presented below.

The published $D(R-H)$ values are listed in Table 1. They were determined by voltammetry¹ with an error of ± 8 kJ mol⁻¹. Reliability of these data was discussed earlier.¹ Table 1 also lists the available enthalpies of formation of starting molecules RH ($\Delta H_f^\circ(RH)$) which were used to calculate the $\Delta H_f^\circ(R^\bullet)$ values. The enthalpies of formation of other compounds RH were evaluated in this work. For instance, the $\Delta H_f^\circ(4)^*$ value was obtained by adding a triple increment of the $-CH_2-$ group (a commonly accepted¹⁵ notation is $C-(H)_2(C)_2$), which equals -20.9 kJ mol⁻¹,¹⁶ to $\Delta H_f^\circ(3)$. The $\Delta H_f^\circ(11)$ value was determined using the macroincrementing scheme¹⁷ from the following equation

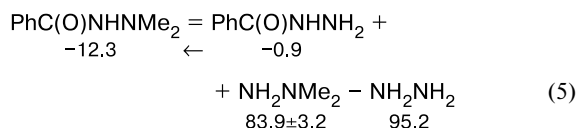
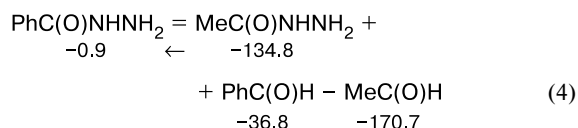
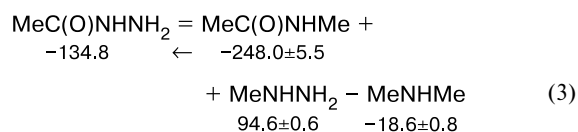
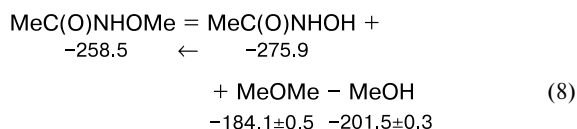
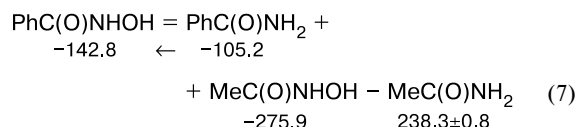
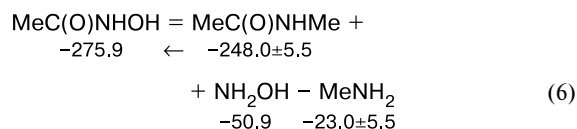


Equation (2) uses the ΔH_f° values of the model compounds PhC(O)NH_2 (5) and MeC(O)NH_2 (2) (see Table 1). The enthal-

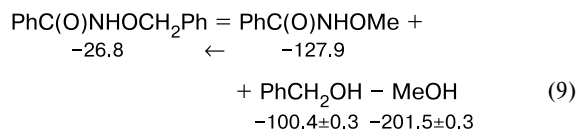
* All compounds are enumerated according to Table 1.

Table 1. Energy characteristics of amidyl radicals R[•] and starting molecules RH (kJ mol⁻¹)

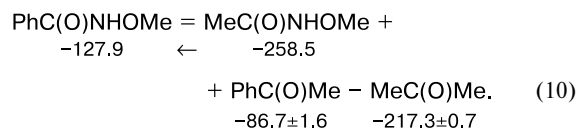
R—H	R [•]	D(R—H)	$\Delta H^\circ_f(\text{RH})$	$\Delta H^\circ_f(\text{R}^\bullet)$		References ¹
				Computational procedure		
				Eq. (1)	QSPR	
1	HC(O)N [•] H	454.0 ⁴	−186 ⁵	50	—	—
2	MeC(O)N [•] H	449.8 ⁴	−238.3±0.8 ⁶	−6.5	2.9	−9
3	Bu ^t C(O)N [•] H	456 ⁴	−313.1±1.4 ⁷	−75	−80.9	—
4	Et ₃ CC(O)N [•] H	456 ⁴	−375.8 ^a	−138	−146.2	—
5	PhC(O)N [•] H	448 ³	−105.2 ^b	125	129.5	122
6	NH ₂ C(O)N [•] H	464 ³	−235.2±1.2 ⁸	11	8.5	1
7	MeC(O)N [•] Me	445.6 ⁴	−248.0±5.5 ⁹	−20.4	−25.1	−4
8	2-Oxopyrrolidin-1-yl	447 ⁴	−197.38±3.05 ¹⁰	32	—	—
9	2-Oxopiperidin-1-yl	458.1 ⁴	−232.1 ^c	8.0 ^d	—	—
10	MeC(O)N [•] Ph ^e	418 ³	−128.9±1.7 ⁶	71	68	68
11	PhC(O)N [•] Ph ^e	406 ³	4.2 ^a	192	195	—
12	MeC(O)N [•] NH ₂	343 ³	−134.8 ^a	−10	−8.3	−37
13	PhC(O)N [•] NH ₂	339 ³	−0.9 ^a	120	118.3	90
14	PhC(O)N [•] NMe ₂	343 ³	−12.3 ^a	113	—	83
15	MeC(O)N [•] OH	368 ³	−275.9 ^a	−130	−132.9	−195
16	PhC(O)N [•] OH	368 ³	−142.8 ^a	7	9.8	−64
17	MeC(O)N [•] OMe	377 ³	−258.5 ^a	−99	−101.8	−169
18	PhC(O)N [•] OCH ₂ Ph	372 ³	−26.8 ^a	127	129.7	59
19	PhC [•] HC(O)NH ₂	357.7 ⁴	−127.6 ^f	12.1	12	—
20	PhC [•] HC(O)NMe ₂	360 ⁴	−133 ^a	9	—	—
21	C [•] H ₂ C(O)NHMe	410 ⁴	−248.0±5.5 ⁶	−56	—	—

^a Calculated in this work (for details of computations and notes, see text).^b Recalculated using the solid-phase ΔH°_f values (-202.14±0.60 kJ mol⁻¹)¹¹ and the enthalpy of sublimation ($\Delta H_{\text{sub}} = 96.6$ kJ mol⁻¹).¹²^c Recalculated using the solid-phase ΔH°_f values (-306.6 kJ mol⁻¹)⁶ and the enthalpy of sublimation ($\Delta H_{\text{sub}} = 74.5$ kJ mol⁻¹).¹³^d Doubtful value (see text).^e $E_c \approx -33$ kJ mol⁻¹.^f Recalculated using the solid-phase ΔH°_f values (-224.0±3.8 kJ mol⁻¹)¹⁴ and the enthalpy of sublimation ($\Delta H_{\text{sub}} = 96.4$ kJ mol⁻¹).¹²pies of formation of compounds **12**–**14** were determined using Eqs (3)–(5).value $\Delta H^\circ_f(\text{NH}_2\text{NH}_2) = 95.2$ kJ mol⁻¹ was taken from Ref. 18. The ΔH°_f parameters of compounds **15**–**18** were calculated using Eqs (6)–(9).

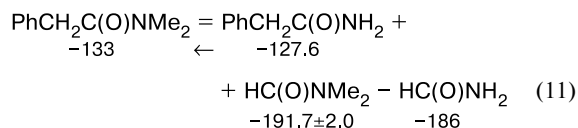
Hereafter, the enthalpies of formation of the model compounds were taken from Ref. 6 unless otherwise specified. The



The ΔH_f° parameter of PhC(O)NHOMe in Eq. (9) was determined from the following relationship



Earlier,² the enthalpies of formation of corresponding compounds were estimated using analogous computational schemes; however, the $\Delta H_f^\circ(\text{RH})$ values for some of the model compounds were outdated and even incorrect (for NH₂OH). In this work for NH₂OH we use a ΔH_f° value of $-50.9 \text{ kJ mol}^{-1}$ taken from Ref. 19. The enthalpy of formation of *N,N*-dimethylbenzylamine (**20**) was determined using Eq. (11).



Results and Discussion

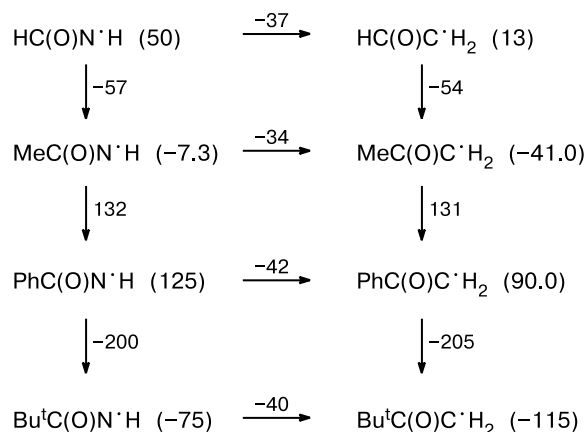
The $\Delta H_f^\circ(\text{R}^\bullet)$ values determined in this work are listed in Table 1. Data verification, consistency studies, and investigations of quantitative structure—property relationships (QSPR) in the series of compounds were carried out using the group additivity scheme implemented in Ref. 1 to study free radicals.

A necessary condition for studies of "structure—enthalpy of formation" relationships is reliability of the reference $\Delta H_f^\circ(\text{R}^\bullet)$ values. The corresponding data set listed in Table 1 meets this conditions, which is indicated by coincidence of the changes in the $\Delta H_f^\circ(\text{R}^\bullet)$ values obtained upon modification of the radical structures (Scheme 1).

The equal "shifts" of $\Delta H_f^\circ(\text{R}^\bullet)$ upon horizontal transitions from $\text{R}^i\text{C(O)N}^\bullet\text{H}$ to $\text{R}^i\text{C(O)C}^\bullet\text{H}_2$ indicate a weak (or identical) influence of the radical center on the residue, R^i . This is confirmed by equality of the vertical "shifts" upon replacement of R^i by R^j (a detailed quantum-chemical study of this effect is now in progress). Of the whole set of the $\Delta H_f^\circ(\text{R}^\bullet)$ values listed in Table 1 two values, for the radicals of compounds **8** and **9**, cast some doubt. The difference between them is smaller than usual values for the five- and six-membered cyclic radicals R^\bullet .

A set of the model fragments employed to simulate the structure of the radicals in question is listed in Table 2. Most of them were considered earlier¹ in the studies of other classes of radicals. Here, these fragments are characterized by the previously found contributions to $\Delta H_f^\circ(\text{R}^\bullet)$. In this work we (i) refined the increments of

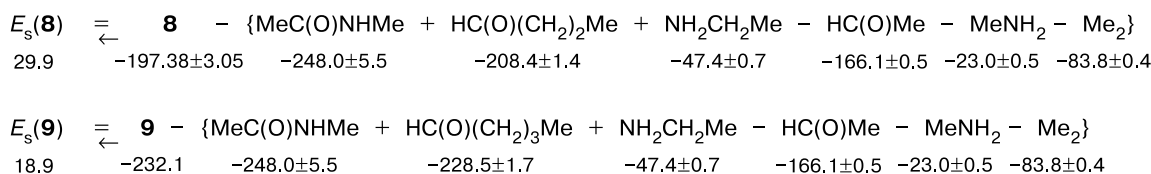
Scheme 1



Note. Listed in parentheses are the ΔH_f° (kJ mol⁻¹) parameters of the corresponding radicals. The "shifts" of the $\Delta H_f^\circ(\text{R}^\bullet)$ values on going from $\text{R}_1^\bullet \rightarrow \text{R}_2^\bullet$ are shown on the right of the arrows.

the $\text{N}^\bullet\text{—(H)(C)}$ and $\text{N}^\bullet\text{—(C)}_2$ groups for which only rough estimates were reported¹ and (ii) first determined the increment of the $\text{C(O)—(N}^\bullet\text{)(C)}$ group and the $E_c(\text{Ph—N}^\bullet\text{C(O)})$ value, or the contribution of the conjugation energy of free electron of carboxyamidyl nitrogen with the π -system of the benzene ring, to $\Delta H_f^\circ(\text{R}^\bullet)$. Structures of the $\text{R}^1\text{C(O)N}^\bullet\text{R}^2$ type are known²⁰ to exhibit mesomerism of the peptide bond, which is responsible for planarity of the —C(O)NH— fragment. This effect can also manifest itself in radicals. Based on this fact and following the group definition,¹⁵ in the framework of the approach in question¹ one should distinguish between the fragments $\text{N}^\bullet\text{—(X)(C)}$ and $\text{N}^\bullet\text{—(X)(CO)}$ ($\text{X} = \text{H}$ or C). Quantitatively, this difference can be estimated as an increment of the CO—(N)(C) group, which was done in this work. The increments were determined by solving the inverse problem by the least squares method. A number of groups listed in Table 2 are characterized by figures in parentheses, which represent tentative estimates of the corresponding increments obtained using the exclusive reference $\Delta H_f^\circ(\text{R}^\bullet)$ values. In three cases, we determined the total increments of combinations of groups; these are the contributions of the $\text{H}_2\text{NN}^\bullet\text{—}$, $\text{HON}^\bullet\text{—}$, and $(\text{C)—ON}^\bullet\text{—}$ fragments linked to the C(O) unit to the corresponding $\Delta H_f^\circ(\text{R}^\bullet)$ values (see Table 2). A comparative analysis of the data listed in Table 2 and the parameters reported in Ref. 1 revealed a decrease in the contributions upon replacement of C by C(O) in the nearest environment (increments of the groups —NH_2 , —NH— , and $>\text{N—}$). The absolute value of the conjugation energy of free electron in the system Ph—N^\bullet also decreases upon introduction of the C(O) group to position 2 relative to N^\bullet , because the radicals $\text{Ph—N}^\bullet\text{H}$ are characterized by

Scheme 2



$E_c(\text{Ph}-\text{N}^\bullet) = -58.1 \text{ kJ mol}^{-1}$.¹ On the contrary, the contributions of the C(O)—(N)(C) and C(O)—(H)(N) groups to $\Delta H_f^\circ(\text{R}^\bullet)$ increase as compared to those of the C(O)—(C)₂ and C(O)—(H)(C) groups.¹ Noteworthy are close values of the ring strain energies (E_s) of the five- and six-membered cyclic radicals of compounds **8** and **9** (~40 and 38 kJ mol⁻¹, respectively). For comparison, consider the E_s values of molecules **8** and **9** calculated using the macroincrementing scheme as the differences between the ΔH_f° values of a real molecule and its hypothetical unstrained analog built of the fragments of the model compounds (shown in braces) (Scheme 2).

The ΔH_f° of the model compounds shown in Scheme 2 were taken from Ref. 6 or from the references listed in Table 1. Since the five- and six-membered cyclic molecules and radicals must be characterized by similar E_s

values,²¹ the ring strain energy of 2-oxopiperidin-1-yl seems to be overestimated. Therefore, in accord with the data severity categories¹ the $\Delta H_f^\circ(\mathbf{9})$ value should be considered doubtful. For the same reason, other $\Delta H_f^\circ(\text{R}^\bullet)$ values listed in Table 1 should be considered experimental. This conclusion and the need for additional studies are confirmed by comparison of the $\Delta H_f^\circ(\text{R}^\bullet)$ values obtained in this work and earlier.² We had to revise eight out of the twelve $\Delta H_f^\circ(\text{R}^\bullet)$ values. In all cases, the reason is the necessity of refining the old values and publication of new ΔH_f° values of either the source or model molecules. The data listed in Table 1 seem to be reliable because they provide reasonable agreement between the $\Delta H_f^\circ(\text{R}^\bullet)$ calculated using the QSPR parameters listed in Table 2 and those determined from experimental $D(\text{R}-\text{H})$ values. A joint analysis of the results obtained suggests that the $\Delta H_f^\circ(\text{R}^\bullet)$ values found in this work using the experimental $D(\text{R}-\text{H})$ values were determined with an error of 8 to 10 kJ mol⁻¹.

Thus, in this study we first determined the ΔH_f° values of nine amidyl radicals and refined those of eight amidyl radicals. The "structure—enthalpy of formation" relationships established here using the group additivity scheme indicate reliability of the $\Delta H_f^\circ(\text{R}^\bullet)$ obtained and the group increments determined permit evaluation of ΔH_f° values for currently uncharacterized radicals.

Table 2. Increments of various atomic groups used for calculations of $\Delta H_f^\circ(\text{R}^\bullet)$ values of amidyl radicals

Group ^a or combination of groups ^b	Increment ^c /kJ mol ⁻¹
N [•] —(H)(C)	207.4
N [•] —(C) ₂	220.5
C [•] —(H) ₂ (C)	148.79 ¹
C [•] —(H)(C) ₂	154.60 ¹
C(O)—(N)(C)	-163.5
C(O)—(H)(N)	(-157.4)
C—(H) ₃ (C)	-41.04 ¹
C—(H) ₂ (C) ₂	-21.76 ¹
C—(C) ₄	-1.67 ¹
C _B —(H)(C _B) ₂	13.8 ¹
C _B —(C)(C _B) ₂	16.6 ¹
$E_c(\text{Ph}-\text{C}^\bullet)$	-29.3 ¹
$E_c(\text{Ph}-\text{N}^\bullet\text{C(O)})$	-33
N—(H) ₂ (CO)	(-35.4)
N—(H)(CO)(C)	(0)
N—(CO)(C) ₂	(43.7)
{N—(H) ₂ (N)} + {N [•] —(N)(CO)}	196.2
{O—(H)(N)} + {N [•] —(O)(CO)}	87.7
{O—(C)(N)} + {N [•] —(O)(CO)}	143.8

^a For notations of groups, see Ref. 15; C_B stands for a benzene ring carbon. Listed are also the E_c values used in calculations of the $\Delta H_f^\circ(\text{R}^\bullet)$ values.

^b See text.

^c The increments estimated using the exclusive $\Delta H_f^\circ(\text{R}^\bullet)$ value are given in parentheses.

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