Calculations of enthalpies of formation of carbenes in the ground state in the gas phase

Yu. D. Orlov,[a]* *Yu. A. Lebedev,*[a] *L. G. Menchikov,*[b] *and O. M. Nefedov*[b]*

[a]*Institute of Chemistry of Nonaqueous Solutions, Russian Academy of Sciences,*
1 ul. Akademicheskaya, 153018 Ivanovo, Russian Federation.
Fax: 007 (093 2) 37 8509
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 117913 Moscow, Russian Federation.
Fax: 007 (095) 135 5328

Known enthalpies of formation ($\Delta_f H^\circ$) of carbenes in the ground state in the gas phase were analyzed; the prospects for the theoretical evaluation of $\Delta_f H^\circ$ were considered. The $\Delta_f H^\circ$ values of carbenes were calculated by the group-addition method, developed previously for free radicals, as well as by the AM1 and PM3 quantum-chemical methods; these methods were compared.

Key words: carbenes, enthalpy of formation; group-addition method; quantum-chemical calculations.

Carbenes are one of the main classes of intermediates formed in chemical reactions.[1] Experimental determination of thermochemical characteristics of carbenes is difficult, because these species are highly reactive and have short lifetimes. Therefore, most of the experimental values known for these compounds have been obtained by indirect methods and often differ substantially from one another. Hence, the development of reliable theoretical methods for the calculation of thermochemical characteristics of carbenes is an important aspect of the studies of reactions involving these species.

Previously, two of us have composed a data bank of thermochemical characteristics of free organic radicals[2,3] and have developed group-addition methods for the calculation of enthalpies of their formation.[4,5] In the present study we calculated enthalpies of formation of carbenes in the ground state using the group-addition method and the AM1 and PM3 quantum-chemical methods and compared the values obtained.

There are literature data[1,6,7] on the compilation of the thermodynamic properties of simple carbenes. Enthalpies of formation for 42 carbenes have been reported in a known monograph;[8] however, it is impossible to distinguish the values obtained experimentally from those calculated by the author using methods based on substitution increments and isodesmic reactions, because the tables given in the monograph are not accompanied by references. Furthermore, some of the experimental values have been corrected by the author of Ref. 8, but this is not reflected in the tables. Therefore, the $\Delta_f H^\circ$ values reported in the monograph under consideration[8] should be used with certain care.

The available experimental data on the enthalpies of formation of carbenes are summarized in Table 1. This table also presents data taken from handbooks[1,6,7] including weighted average values and the results of numerical estimates as well as a number of values taken from the monograph mentioned above.[8] Some of the data listed in Table 1 are characterized by large errors or have been obtained using rough approximations. For example, the $\Delta_f H^\circ$ values for $^1CBr_2$, $^1CI_2$, and ^3CHPh were found from a comparative examination of the enthalpies of formation of carbenes and of radicals having similar structures. All the foregoing complicates markedly the task of analysis, correlation, and interpretation of the data presented.

To calculate $\Delta_f H^\circ$ by the group-addition approach, we chose the values, most reliable from our viewpoint, among the enthalpies of formation of carbenes (see Table 1) and used them as reference values. Table 1 also includes the multiplicities of the ground states of carbenes. Although not all of the values listed in Table 1 correspond in reliability to reference values, it is quite admissible to use the present set of $\Delta_f H^\circ$ in order to verify whether this method can be employed and whether this leads to trustworthy results. However, the set of reference values in question is inadequate for the group-addition method to be used for the calculation of the $\Delta_f H^\circ$ values of carbenes of various structures. This problem can be solved by assuming that the effects of identical substituents on free-radical and carbene centers are quantitatively close to one another. This would make it possible to reduce the task to the transfer to carbenes of the well-developed group-addition method

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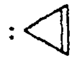
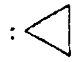
Table 1. Experimental and calculated enthalpies of formation ($\Delta_f H^\circ$) of carbenes

Carbene	Multiplicity of the ground state	$\Delta_f H^\circ$/kJ mol^{-1}			
		experiment	the group-addition method	AM1	PM3
CH_2	3	390.4±4.0[7]	—	337.8	316.2
CF_2	1	−180.0±10,[7] −205±12,[9] −164.8±14.2[10]	−158.1	−284.1	−205.2
CHF	1	105.3±25,[7] 109±12,[9] 163.1,[11] 157±18[12]	147.9	87.3	147.4
CCl_2	1	226.2±20,[7] 163±12,[9] 230±8,[13] 218.0±14.2,[10] 213.4±8.4[14]	197.8	202.5	240.1
CHCl	1	308.3±30,[7] 298±21,[9] 317±20[12]	319.7	324.6	347.7
CFCl	1	25±20,[7] −8±29,[9] 24*	18.3	−15.9	43.1
CBr_2	1	336.6±50[7]	315.1	376.3	438.7
CHBr	1	373±18[12]	382.2	412.7	459.7
CFBr	1	63*	80.8	77.6	112.4
CI_2	1	468.4±60,[7] 503.3[8]	419.3	508.3	508.2
CHI	1	428±21[12]	434.3	496.0	489.0
$C{=}CH_2$	1	397.0±14.6[17]	—	471.8	453.2
C=C=O	3	290.8[6]	—	407.6	367.9
C=NH	1	175.3,[18] 179.9[8]	—	204.1	236.6
	1	477±17[19]	543.0	621.7	569.2
$C{=}C{=}CH_2$	1	502−523[20]	—	587.6	582.6
CHC≡CH	3	586[20]	572.9	515.9	505.7
CHMe	3	366 1[8]	342.8	277.7	252.4
	1	450.6[8]	384.5	506.0	478.4
CHC≡N	3	460±100[15]	480.0	459.1	465.0
$CFCF_3$	1	−586±12[21]	−580.4	−574.5	−528.5
CFC_2F_5	1	−1008±21[21]	−996.4	−964.3	−940.3
$C(CF_3)_2$	3	−887±21[22]	−887.2	−941.0	−964.8
$C(CF_3)C_2F_5$	3	−1305±12[21]	−1304.9	−1330.2	−1374.7
CPhH	3	427[8]	440.1	430.5	418.9

(to be continued)

Table 1. *(continued)*

Carbene	Multiplicity of the ground state	$\Delta_f H°$/kJ mol^{-1}			
		experiment	the group-addition method	AM1	PM3
CPhF	1	114.2[23]	108.5	157.5	196.9
CPhCl	1	280.7[23]	280.3	375.4	386.5
CPhBr	1	333.9[23]	342.8	455.1	474.5
CPh_2	3	364.0[24]	512.0	497.9	493.3
C(F)OMe	1	−234÷−222[23]	−228.1	−260.4	−225.8
C(Cl)OMe	1	−90.4[25]	−90.2	−2.1	14.6
$C(OMe)_2$	1	−255[25]	−302.7	−244.9	−228.1
CFI	1	—	133	153.8	154.7
CClBr	1	—	253	292.3	321.4
CClI	1	—	305	372.8	356.2
CBrI	1	—	367	438.3	473.5
CMe_2	3	—	296	221.1	195.7
$CHNH_2$	1	—	351	369.0	393.0
$C(NH_2)C{\equiv}N$	1	—	352	309.8	341.1
$C(F)C{\equiv}N$	3	—	268	227.6	276.7
CHOH	1	—	67	69.6	68.4
CHCHO	3	—	275	202.6	167.0
CHCOOH	3	—	33	−39.2	−60.6
C(Me)OMe	1	—	−63	38.1	31.4
C(Cl)OPh	1	—	70	163.7	161.1
$C(CF_3)C(O)CF_3$	3	—	−1021	−1053.7	−1097.2
$C(CF_3)C(O)C_2F_5$	3	—	−1439	−1435.5	−1497.2
$CHCF_3$	3	—	−245	−319.7	−342.4
$CHCH{=}CH_2$	3	—	395	364.7	356.6
CBu^t_2	3	—	128	124.4	80.6
$C(CF_3)Ph$	3	—	−198	−220.3	−233.4

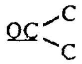
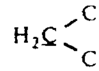
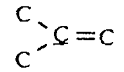
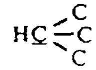
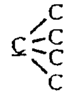
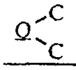
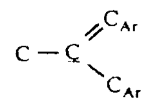
Note. When several dissimilar experimental $\Delta_f H°$ values have been reported, we chose the most reliable of them (underlined) and used it in the subsequent calculations as the reference value.
* These values were estimated by us based on the reported bond dissociation energies (data of Ref. 15) and enthalpies of formation of carbynes CF and CCl (data of Ref. 16).

for the calculation of the $\Delta_f H°$ values of free organic radicals. In this study, we used the first approximation[4,5] of this approach, developed for free organic radicals. According to this approximation, the contributions of groups in free radicals to the enthalpies of formation were taken as the contributions of the corresponding groups containing no carbene center to $\Delta_f H°$. Thus, the values of $\Delta_f H°$ of carbenes XYC in the ground state were calculated from the following formula

$$\Delta_f H°(XYC) = C_c + \sum_i A_i + E_S + E_C + \sum_{k,l} \Delta_{k,l}, \qquad (1)$$

where C_c is the contribution of the carbene center; A_i are the contributions of other groups in the carbene; E_S is the

Table 2. Contributions (kJ mol^{-1}) of various groups (underlined) to $\Delta_fH°$ of radicals and carbenes

Group	Contribution	Group	Contribution	Group	Contribution	Energy	Contribution
$H_3\underline{C}-C$	−41.0		−134.2	$(C)-H\underline{C}=C$	35.6	$\Delta_{1,1}(F-F)^a$	−4.6
	−21.8	$H\underline{CO}-(C)$	−135.9		38.9	$\Delta_{1,1}(Cl-Cl)^a$	7.7
	−13.4	$\underline{NC}-(C)$	96.1	$C=\underline{C}=C$	67.9	$\Delta_{1,1}(Br-Br)^a$	0
	−1.7	$H_2\underline{N}-(C)$	−2.3	$H\underline{C}\equiv C$	107.9	$E_S(C\equiv C-C^{\cdot})^b$	−36.5
$H\underline{O}-C$	−175.3	$\underline{F}-(C)$	−205.7	$(C)-\underline{C}\equiv C$	117.7	$E_S(C=C-C^{\cdot})^b$	−52.0
	−128.4	$\underline{Cl}-(C)$	−33.9	$H\underline{C}_{Ar}-(C_{Ar})_2$	13.8	$E_S(C_6H_5-C^{\cdot})^b$	−29.3
		$\underline{Br}-(C)$	28.6		16.6		
		$\underline{I}-(C)$	80.7				
		$H_2\underline{C}=C$	27.2				

Note. The atoms linked directly to the central atom of the group under consideration are given in parentheses after the dashes; C_{Ar} is a carbon atom belonging to a benzene ring.

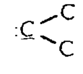
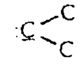
* These values were estimated by us based on the reported bond dissociation energies (data of Ref. 15) and enthalpies of formation of carbynes *CF* and CCl (data of Ref. 16).

energy of conjugation of the free electrons of the carbene center with the π-system in conjugated carbenes; E_C is the ring strain energy in cyclic carbenes; and $\Delta_{k,l}$ is the energy of nonvalent electrostatic interactions between electronegative atoms and groups in substituents.

The C_c values for Eq. (1) are found using reference $\Delta_fH°$ values, while the other terms in this equation are parameters characterizing structural fragments, which were reported previously[4,5] in the studies dealing with the development of the first approximation of the approach in question. To present the structural parameters, we used the generally accepted designations for groups[29—31] (Table 2). In terms of the first approximation, it was assumed that the contributions of identical groups to the enthalpies of formation of the intermediates are equal, irrespective of the distance (along the chain in the species) between this group and an atom with unpaired electrons. Based on the experimental values of $\Delta_fH°$ of carbenes (see Table 1), we calculated the contributions of the HC: and C: centers to $\Delta_fH°$, which are determined taking into account the multiplicity of the ground state of the corresponding carbene (Table 3). These parameters were calculated with different degrees of reliability. They can be made more accurate following the appearance of new reference $\Delta_fH°$ values for carbenes and the refinement of the existing values. Some $\Delta_fH°$ values of carbenes, calculated by the method described above, are also listed in Table 1. The $\Delta_fH°$ values for those carbenes for which no experimental $\Delta_fH°$ are available but the multiplicity of the ground state is known[1,6,7] were calculated by the group-addition method in a similar way (see Table 1). We did not consider cyclic conjugated carbenes, because the calculation of $\Delta_fH°$ for these species requires additional data on the E_C and E_S values. Table 1 also includes the enthalpies of formation of carbenes that we found by the AM1 and PM3 semiempirical quantum-chemical calculations (see Ref. 26) using the MOPAC program with full optimization of the molecular geometry.

Comparison of the $\Delta_fH°$ values calculated by different methods for singlet halocarbenes (Figs. 1—3) and triplet carbenes (Fig. 4) indicates that the values obtained by the group-addition method are closer to experimental results than those found by quantum-chemical calculations. In general, the enthalpies of formation of halocarbenes obtained by the group-addition method lie within the confidence intervals of the corresponding experimental values. In the calculation of $\Delta_fH°$ for cyclopropenylidene, we used the E_C and E_S values for the cyclopropenyl radical;[5] however, this proved to be improper, because, according to the published data,[27] the p-orbital of the carbene center in cyclopropenylidene is involved in the common π-system of the three-membered ring. In addition, the bond angle at the carbene center in cyclopropenylidene is smaller than that in

Table 3. Group contributions (C_c) of carbene centers (underlined) to $\Delta_fH°$ of carbenes

Group	Multiplicity of the ground state	C_c /kJ mol^{-1}
	1	257.9
	3	377.9
$:\underline{C}H-C$	1	353.6
$:\underline{C}H-C$	3	383.8

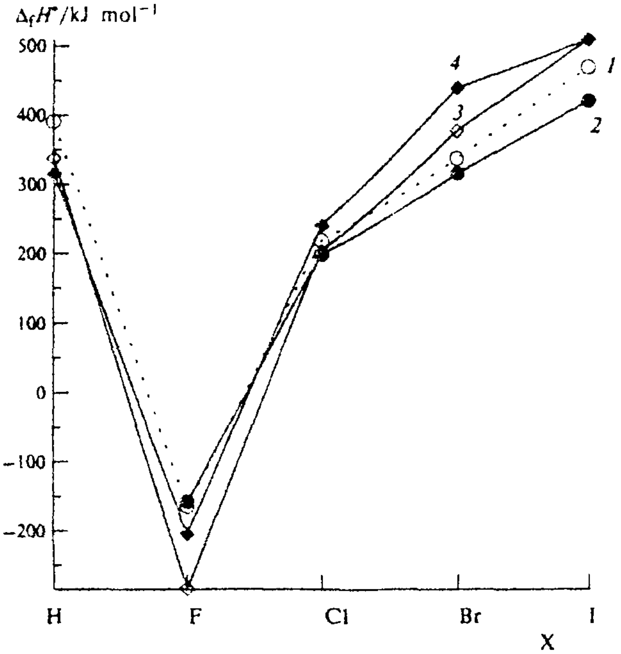


Fig. 1. Dependence of the enthalpies of formation ($\Delta_f H^\circ$) of singlet carbenes CX_2 on the substituent X (here and below, *1*, experimental values; *2*, the results of the group-addition method; *3*, AM1 calculations; and *4*, PM3 calculations).

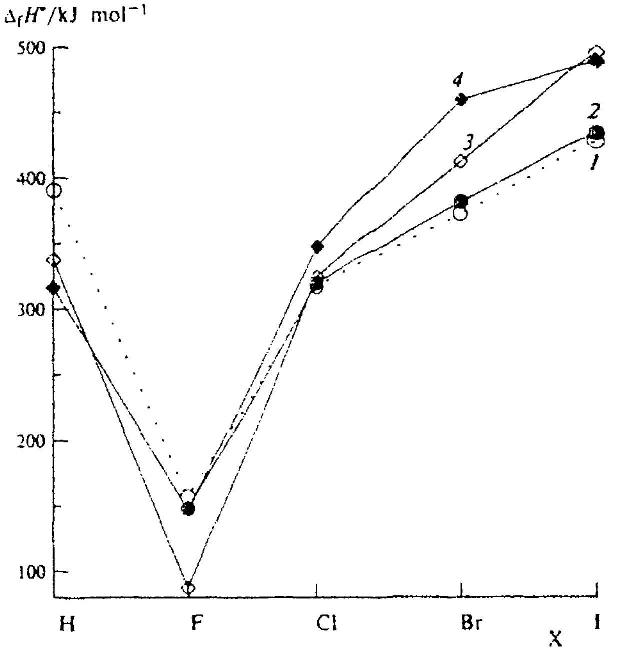


Fig. 2. Dependence of the enthalpies of formation ($\Delta_f H^\circ$) of singlet carbenes CHX on substituent X (for notation, see Fig. 1).

methylene; consequently, a zwitterion type singlet state is stabilized, and cyclopropenylidene has the structure of an onium anion. Similarly, the substantial underestimation of the $\Delta_f H^\circ$ value calculated for cyclopropylidene can be explained by the fact that the CH—C—CH bond angle in the singlet ground state of this carbene is 6—7° smaller than that in the triplet state (see Ref. 27). Therefore, the structure of singlet cyclopropylidene is additionally strained, and the $\Delta_f H^\circ$ value increases. If we assume that the energies of this strain in cyclopropenylidene and cyclopropylidene are identical and are equal to ≈66 kJ mol^{-1} (see Table 1), the energy of the additional stabilization of cyclopropenylidene, due to the change in its structure, should be ≈130 kJ mol^{-1}. In the calculation of $\Delta_f H^\circ$ for diphenylcarbene, $^3CPh_2$, we used the value $E_S(CHPh_2)$ = −31.7 kJ mol^{-1} (see Ref. 5). At the same time, it should be expected that the energy of conjugation in this carbene will increase, because the Ph—C—Ph angle at the central carbon atom in this case (150°, see Refs. 1, 7) is larger than that in the corresponding free radical $CHPh_2$ (the Ph—C—Ph angle is 120°, see Ref. 5).

The fact that for some carbenes, the $\Delta_f H^\circ$ values, calculated by the method of group contributions, deviate markedly from the experimental values is due, as a rule, to some specific features of their structures; this is confirmed once again by the above examples. The effects of these specific features on the $\Delta_f H^\circ$ values are normally taken into account by introducing additional parameters. For example, stabilization of the singlet

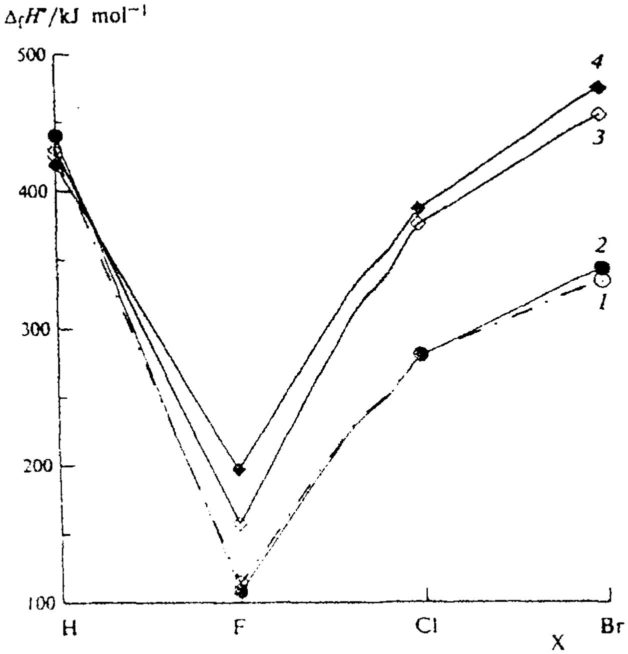


Fig. 3. Dependence of the enthalpies of formation ($\Delta_f H^\circ$) of singlet carbenes CPhX on substituent X (for notation, see Fig. 1).

states of methoxycarbenes $^1C(F)OMe$ and $^1C(Cl)OMe$ is ensured by the interaction of the unshared electron pair of the O atom with the vacant p-orbital at the

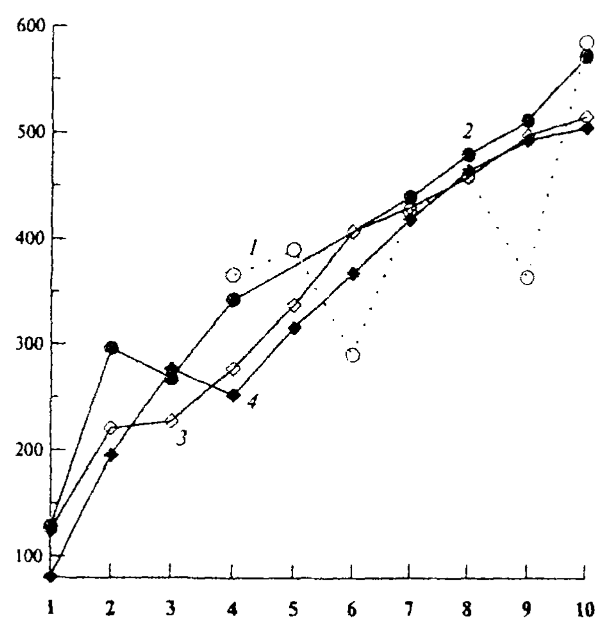


Fig. 4. Enthalpies of formation ($\Delta_f H^\circ$) of triplet carbenes $C(CMe_3)_2$ (1), CMe_2 (2), $C(F)C{\equiv}N$ (3), CHMe (4), CH_2 (5), C=C=O (6), CHPh (7), $CHC{\equiv}N$ (8), CPh_2 (9), and $CHC{\equiv}CH$ (10) (for notation, see Fig. 1).

carbene center.[28] For this reason, when the $\Delta_f H^\circ$ values of these carbenes are calculated using standard parameters (see Tables 2 and 3), the results deviate substantially from experimental values. When the additional energy of conjugation E_S(O...C), which is equal to −110.9 kJ mol^{-1} in conformity with the first approximation for free radicals,[5] is taken into account, the $\Delta_f H^\circ$ values calculated for C(Hal)OMe are in good agreement with experimental data. In this case, as in the case of free radicals, the E_S value is not additive, since $E_S(O...C...O) \neq 2E_S(O...C)$. This can be seen using dimethoxycarbene $^1C(OMe)_2$ as an example (see Table 1). Note once again that all the calculations performed refer to carbenes in the ground state. The determination of the multiplicity of the ground states of carbenes presents a separate, rather complex problem.[1]

Thus, the results of the performed calculations, their comparison with experimental data, and the rationalization of the large deviations observed indicate that the group-addition method for the calculation of $\Delta_f H^\circ$ is applicable to carbenes in the ground state.

Analysis of the results of AM1 and PM3 semiempirical quantum-chemical calculations (see Table 1) for halocarbenes CX_2, CHX, and CPhX (see Figs. 1—3, respectively) indicates that these methods lead to underestimation of $\Delta_f H^\circ$ values for fluorocarbenes and to overestimation of these values for the rest of the halocarbenes, and these errors are systematic. In general, for the ten carbenes in the triplet ground state studied (see Fig. 4), the calculated values are in satisfactory agreement with the experimental data. The most accurate $\Delta_f H^\circ$ values for singlet carbenes are obtained by the AM1 method, those for fluorocarbenes are found by the PM3 method, and in the case of triplet carbenes, the most accurate results are provided by the AM1 method. Thus, as a rule, quantum-chemical methods understate the $\Delta_f H^\circ$ values of triplet carbenes and, conversely, overstate $\Delta_f H^\circ$ for singlet carbenes, all these methods being characterized by large scattering of the results obtained. Quantum-chemical methods are appropriate, most of all, in the case of the calculation of $\Delta_f H^\circ$ values for carbenes having some specific geometrical or electronic features, for which no data on the corresponding group contributions have been reported.

Analysis of the $\Delta_f H^\circ$ values found by various methods provides reasons for critical evaluation of the existing experimental enthalpies of formation of a number of carbenes. For example, in the case of diphenylcarbene (triplet ground state), calculations lead to $\Delta_f H^\circ$ lying in the 494—512 kJ mol^{-1} range, which indicates that the experimental[24] value, equal to 364.0 kJ mol^{-1}, must be checked and determined more accurately.

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