Determination of enthalpies of formation of organic free radicals from bond dissociation energies
2.* Halosubstituted radicals

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The enthalpies of formation (ΔH_f°) for 23 halosubstituted radicals were determined from the published data on bond dissociation energies. The ΔH_f° values of the corresponding molecules necessary for the calculation of ΔH_f° of the radicals were taken from handbooks or calculated by the additive-group method. The conjugation energies of the radicals are calculated, and the effect of substituents at the π-system on these values was shown. Errors of determination of the ΔH_f° values of the radicals were estimated.

Key words: thermochemical properties, halosubstituted radicals, calculations of properties.

An approach to the determination of the enthalpy of formation (ΔH_f°) of organic free radicals ($R^\cdot$) has been described previously.[1] It is based on selection of published values of the dissociation energy (D) of R—X bonds in RX molecules, for which the corresponding $\Delta H_f^\circ(R^\cdot)$ values are absent. In this case, the problem of determination of $\Delta H_f^\circ(R^\cdot)$ is reduced mainly to determining the enthalpies of formation of molecules, $\Delta H_f^\circ(RX)$. Except where especially mentioned, we consider the enthalpy of formation of a compound in the ideal gas state and under standard thermodynamic conditions.

In this work, the approach indicated was applied to the determination of ΔH_f° of halosubstituted radicals. The state of the modern databank of $\Delta H_f^\circ(R^\cdot)$ values has been briefly characterized as a whole.[1,2]

Let us begin our study by a specific consideration of halosubstituted ethyl radicals characterized more completely by their ΔH_f° values than other halosubstituted hydrocarbon radicals. However, this is mainly related to F- and Cl-substituted ethyl radicals. The enthalpy of formation of 1,1,2,2-tetrafluoro-2-chloroethyl (-686 ± 17 kJ mol^{-1}) has been determined[3] from the value $D(ClF_2CCF_2—Cl) = 326\pm 8$ kJ mol^{-1} found in the experimental study of exchange reactions. This value was recommended as a reference in Ref. 4. We corrected it on the basis of a new value of $\Delta H_f^\circ(ClF_2CCF_2Cl)$[5] to obtain -721 ± 9 kJ mol^{-1}, which differs substantially from the accepted value. The corresponding calculation was performed by the correlation

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

All values mentioned are presented in Table 1. Based on the $D(BrF_2CC^\cdot F_2—Br)$ value determined[9] in the study of the thermal decomposition of 1,2-dibromo-1,1,2,2-tetrfluoroethane in a single-pulse impact tube, we obtained the ΔH_f° value for the $BrF_2CC^\cdot F_2$ radical. The corresponding values are also presented in Table 1. The calculation of ΔH_f° for 2-iodo-1,1,2,2-tetrafluoroethyl from Eq. (1) is based on the value $D(IF_2CCF_2—I) = 381$ kJ mol^{-1},[10] which was obtained by mass spectrometry. However, it is unreasonably low. In fact, the analysis of the D(C—F) values in a series of molecules shows[4,19] that they do not include values lower than 440 kJ mol^{-1}. In addition, the comparison of ΔH_f° for $ClF_2CC^\cdot F_2$, $BrF_2CC^\cdot F_2$, and $IF_2CC^\cdot F_2$ radicals shows (see Table 1) that ΔH_f° ($IF_2CC^\cdot F_2$) is close to ΔH_f° ($ClF_2CC^\cdot F_2$). This contradicts the regularity of changing ΔH_f° in the series of halosubstituted methyls, which can be observed in the literature.[19] According to this regularity, for consecutive substitution by F, Cl, Br, and I, the ΔH_f° value increases monotonically. Taking into account the accepted[4] value $\Delta H_f^\circ(F_3CC^\cdot F_2) = -892.9$ kJ mol^{-1}, the regularity is also fulfilled in the series considered except $\Delta H_f^\circ(IF_2CC^\cdot F_2)$. However, if the $D(IF_2CCF_2—F)$ value is taken to be 480 kJ mol^{-1}, *i.e.*, close to D(C—F) in molecules with similar structures,[19] we obtain a $\Delta H_f^\circ(IF_2CC^\cdot F_2)$ value correspond-

* For Part 1, see Ref. 1.

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

R	X[a]	$D(R-X)$	$\Delta H_f^\circ(RX)$	$\Delta H_f^\circ(R)$[b]	$\Delta H_f^\circ(R)$[c] (calc.)	$-E_s$[d]
$ClF_2CC^\bullet F_2$	Cl	326±8 [3]	−925.2±4.3 [5]	−721[e]	−706.6	0
$BrF_2CC^\bullet F_2$	Br	278 [9]	−789.9±4.0 [5]	−624	−644.1[f]	0
$IF_2CC^\bullet F_2$	F	(381) [10 g]	−1011.4 [5 h]	(−710)[g]	−592	0
$F_3CC^\bullet HCl$	Br	274.9±6.3 [4]	−699.9±3.8 [5]	−536.8[i]	−545.3[j]	0
$F_3CC^\bullet HCl$	H	425.9±6.3 [4]	−746.4 [5 h]	−538.5	—	0
$F_3CC^\bullet Cl_2$	Cl	308.0 [12]	−725.3 [5 h]	−538.6	−567.6[j]	0
			−778.3[h]	−591.6		
$F_3CC^\bullet ClBr$	H	404.2±6.3 [4]	−699.9±3.8 [5]	−513.7[i]	−512.9[j]	0
$F_3CC^\bullet ClBr$	Br	251.0±6.3 [4]	−634.2 [5 h]	−495.0	—	0
$(F_3C)_2C^\bullet F$	H	433 [13]	−1565.6[h]	−1351	—	0
$MeCH_2C^\bullet Br_2$	Br	254.3 [12]	3.5[h]	146.0	155.4	0
$ICH_2CH_2C^\bullet H_2$	I	227.7 [12]	48.8[h]	169.7	185.7	0
$ClCH_2CH{=}CHC^\bullet H_2$	Cl	280.5 [12]	−55.3[h]	103.9	—	−60.1
$CH_2{=}CHC^\bullet HF$	H	370.7±4.6 [14]	−156.3[h]	−3.6	—	−15.3
$CH_2{=}CHC^\bullet HCl$	H	370.7±4.6 [14]	−0.6 [15]	152.1	—	−31.4
$CH_2{=}CHC^\bullet HBr$	H	374.0±4.6 [14]	45.2±4.2 [16]	201.2	—	−45.0
$HClC{=}C^\bullet Cl$	H	448±8 [17]	4.6±8.5 [16]	235	—	0
$FClC{=}C^\bullet Cl$	H	452±8 [17]	−196.7[h]	37	—	0
$F_2C{=}C^\bullet Cl$	H	456±8 [17]	−331.4 [15]	−93	—	0
$HFC{=}C^\bullet F$	H	460±8 [17]	−332.2[h]	−90	—	0
$F_2C{=}C^\bullet F$	H	464±8 [17]	−490.4±8.4 [16]	−244	—	0
p-$FC_6H_4C^\bullet H_2$	H	374.0 [18]	−147.5±1.1 [16]	10.5	—	−17.9
p-$BrCH_2C_6H_4C^\bullet H_2$	Br	276.1 [12]	58.7[h]	223.0	—	−20.7
o-$IC_6H_4^\bullet$	I	266.2 [12]	251.7±5.9 [16]	411.1	413.4	0
$PhC^\bullet HCl$	Cl	276.6 [12]	17.8[h]	173.1	—	−33.2
$PhC^\bullet Cl_2$	Cl	278.2 [12]	10.0[h]	166.9	—	−19.6

[a] The following auxiliary values were used: $\Delta H_f^\circ(H) = 218.0$, $\Delta H_f^\circ(F) = 79.5$, $\Delta H_f^\circ(Cl) = 121.3$, and $\Delta H_f^\circ(Br) = 111.8$ kJ mol^{-1}. [b] Calculated from Eq. (1). [c] Calculated from the described[6,7] method. [d] The determination and method for calculation of conjugation energies have been developed previously.[8] [e] Corrected value. [f] According to the refined data, the contribution of Br—(C) is equal to 28.6 kJ mol^{-1}. [g] Underestimated values. For explanation, see text. [h] Calculated values. For explanation, see text. [i] Preferable values. [j] Calculated by the substitution increment method.[11]

ing to this regularity. The $\Delta H_f^\circ(IF_2CC^\bullet F_3)$ value, which was determined from the experimentally measured[5] difference between ΔH_f° for EtI and EtBr and the calculated[5] $\Delta H_f^\circ(EtBr)$ value, was used in the estimations described. For comparison, Table 1 presents the $\Delta H_f^\circ(R^\bullet)_{calc}$ values for the three radicals indicated. These values were calculated using the additive-group method.[6,7] The noticeable deviations of these values from those determined from Eq. (1) can be related to uncertainty of contributions of nonvalence F—Cl and F—Br interactions (in fact, this uncertainty is inherent in the method).[6,7] Nevertheless, the true value of $\Delta H_f^\circ(IF_2CC^\bullet F_2)$ should be close to $\Delta H_f^\circ{}_{calc}$. The errors of the enthalpy of formation of halosubstituted hydrocarbon radicals are twice as large, on the average, as the corresponding errors for unsubstituted analogs. For $\Delta H_f^\circ(ClF_2CC^\bullet F_2)$ and $\Delta H_f^\circ(BrF_2CC^\bullet F_2)$, according to our estimations, they are not lower than ±9 kJ mol^{-1}.

The $D(C-H)$ and $D(C-Br)$ values are presented in Ref. 4 and unpublished data cited herein. Based on these data, we determined ΔH_f° for $F_3CC^\bullet HCl$ and $F_3CC^\bullet ClBr$ radicals according to Eq. (1). All corresponding values are presented in Table 1. Finally, the almost coinciding $\Delta H_f^\circ(F_3CC^\bullet HCl)$ values were obtained from two D values for different bonds. Similar calculations of $\Delta H_f^\circ(F_3CC^\bullet ClBr)$ give values differing by 19 kJ mol^{-1}. This is most likely related to an error in the $\Delta H_f^\circ(F_3CC^\bullet ClBr_2)$ value obtained[5] by calculations. Among the indicated pairs of the $\Delta H_f^\circ(R^\bullet)$ values, we prefer those found using experimental values of ΔH_f° for molecules. The additive-group method for calculation of $\Delta H_f^\circ(R^\bullet)$[6,7] is not developed for polyhalosubstituted hydrocarbons containing two or more different halogens, and its direct application in these cases can lead to a substantial error. In fact, using the known method,[6,7] we obtain −511.9 and 476.9 kJ mol^{-1} for the $F_3CC^\bullet HCl$ and $F_3CC^\bullet ClBr$ radicals, respectively. In this case, the method of substitution increments[11] can be used. In this method, the ΔH_f° values for the radicals indicated are calculated by the substitution scheme

$$F_3CC^\bullet H_2 \longrightarrow F_3CC^\bullet HCl \longrightarrow F_3CC^\bullet ClBr \quad (2)$$

ΔH_f/kJ mol^{-1} −517.1 −28.1 32.4

using $\Delta H_f^\circ(F_3CC^\bullet H_2) = -517.1 \pm 8$ kJ mol^{-1} as the reference value[4] and the modern version of the parameters of the substitution method.[11] The $\Delta H_f^\circ(R^\bullet)_{calc}$ values thus determined (see Table 1) agree satisfactorily with those found from Eq. (1).

Then the $D(i\text{-}C_3F_7\text{—H})$ value obtained[13] by the kinetic method was used. The $\Delta H_f^\circ(F_3CCHFCF_3)$ value was calculated by the additive-group method.[20] The ΔH_f° value for perfluoroisopropyl determined from Eq. (1) is presented in Table 1. Its error is most likely not less than ±12 kJ mol^{-1}, which is related to a considerable error in the method of determination of D.

In the light of the problem stated, the results of Ref. 14, which estimated the dissociation bond energies $D(CH_2CHCHG\text{—H})$, where G is F, Cl, or Br, from the analysis of the data on the kinetics of isomerization of allyl chloride, are of great interest. For all three D values, the error was the same;[14] however, the $D(CH_2CHCHCl\text{—H})$ value can be considered to be most reliable, since published data with different degrees of reliability were used for estimation of the two other D values. The enthalpies of formation of $CH_2{=}CHCH_2Cl$ (see Ref. 15) and $CH_2{=}CHCH_2Br$ (see Ref. 16) molecules were taken from reference books; the $\Delta H_f^\circ(CH_2{=}CHCH_2F)$ value was calculated from the parameters of the additive-group method.[21] All the values mentioned are presented in Table 1. For the radicals considered, the stabilization energies E_s due to conjugation of a free radical with the π-system were estimated using the described procedure and known[8] parameters. The comparison of the values obtained with the E_s value for the allyl radical (−52.0 kJ mol^{-1})[8] shows the noticeable effect of substituents on E_s, which increases as the electronegativity and donor properties increase in the series Br, Cl, and F. According to the aforesaid, we assume different errors of $\Delta H_f^\circ(R^\cdot)$ for the three radicals indicated: ±6.2 kJ mol^{-1} for $CH_2{=}CHC^\cdot HCl$ and $CH_2{=}CHC^\cdot HBr$ and ±8.4 kJ mol^{-1} for $CH_2{=}CHC^\cdot HF$.

The five values of D(C—H) in halosubstituted ethylenes were obtained[17] by studying the exchange reactions by GC. They are presented in Table 1 along with the ΔH_f° values for the corresponding molecules, which were either taken from the cited reference books,[15,16] or calculated from the additive-group method with the parameters from Ref. 21. The ΔH_f° values of the corresponding five radicals presented in Table 1 have errors not less than ±12 kJ mol^{-1}.

The enthalpy of formation of *p*-fluorobenzyl was determined from the $D(CH_2\text{—H})$[18] and $\Delta H_f^\circ(p\text{-}FC_6H_4Me)$[16] values. It is noteworthy that E_s of benzyl decreases (−29.3)[8] when the F substituent is introduced into the benzene ring. A similar decrease in E_s was mentioned above for the allylic type radicals.

Additional challenges for extending the database on $\Delta H_f^\circ(R^\cdot)$ are given by the possibility to determine D from experimental values of rate constants and activation energies of reactions of radical abstraction from the X atom. These reactions proceed *via* the equation

$$R^\cdot + R_iX \longrightarrow RX + R_i^\cdot \qquad (3)$$

This approach is based on the parabolic model of the transition state of reactions (3)[22] and was used[12,23] for determination of more than 100 D values, the majority of which have not been known before. The obtained mass of new data on D was also used for determining new values of $\Delta H_f^\circ(R^\cdot)$. We determined ΔH_f° for eight new radicals of the class considered in this work. The ΔH_f° values of the starting compounds for the CF_3CCl_3 and $o\text{-}I_2C_6H_4$ molecules were taken from the literature.[16] Six ΔH_f° values for other molecules ($MeCH_2CBr_3$, $ICH_2CH_2CH_2I$, $ClCH_2CH{=}CHCH_2Cl$, $p\text{-}BrCH_2C_6H_4CH_2Br$, $PhCHCl_2$, and $PhCCl_3$) were calculated from the additive-group method with the published parameters.[20] All of them, as well as the $\Delta H_f^\circ(R^\cdot)$ values obtained from ΔH_f°, are tabulated (Table 1).

Analysis of the $\Delta H_f^\circ(R^\cdot)$ values determined casts doubt on the reliability of the value $\Delta H_f^\circ(CF_3C^\cdot Cl_2)$ = −538.6 kJ mol^{-1}, because it coincides with $\Delta H_f^\circ(CF_3C^\cdot HCl)$ (see Table 1). Overestimation of the value $\Delta H_f^\circ(CF_3CCl_3)$ = −725.3 kJ mol^{-1}, which was obtained[5] previously by calculation using the paired interaction method, can be a reason for the error. The calculation by the group contribution method[20] gives $\Delta H_f^\circ(CF_3CCl_3)$ = −778.3 kJ mol^{-1}, which coincides with the result (−778.4 kJ mol^{-1}) of a similar calculation from the known parameters.[21] The value of $\Delta H_f^\circ(CF_3C^\cdot Cl_2)$ obtained by a substitution scheme[11] similar to Eq. (2) is presented in Table 1 as the calculated value. At the same time, calculation from the described method[6,7] gives −531.7 kJ mol^{-1}. Unfortunately, at this stage, it is impossible to eliminate the contradictions associated with the $\Delta H_f^\circ(CF_3C^\cdot Cl_2)$ value. For the $\Delta H_f^\circ(R^\cdot)$ values considered, the E_s values of the conjugated radicals (see Table 1) cannot be thoroughly analyzed against the background of errors not less than 12 kJ mol^{-1}. Nevertheless, the introduction of halogens to the β-position relative to the π-bond ($ClCH_2CH{=}CHC^\cdot H_2$ and $p\text{-}BrCH_2C_6H_4C^\cdot H_2$ radicals) has a slight effect on E_s, and a decrease (in modulus) in E_s is observed on going from $PhC^\cdot HCl$ to $PhC^\cdot Cl_2$. The fact that the determined and calculated values of $\Delta H_f^\circ(o\text{-}IC_6H^\cdot{}_4)$ coincide indicates the absence of a noticeable contribution of the *ortho*-interaction of the iodine atom and the σ-type free valence to $\Delta H_f^\circ(R^\cdot)$. The satisfactory correspondence between the calculated $\Delta H_f^\circ(R^\cdot)$ values with those determined in this work also should be mentioned.

The analysis performed allowed us to determine for the first time the enthalpies of formation of 23 halosubstituted hydrocarbon radicals, which comprises more than 30% of the databank of ΔH_f° for these radicals.

References

1. Yu. D. Orlov, R. Kh. Zaripov, and Yu. A. Lebedev, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 637 [*Russ. Chem. Bull.*, 1998, **47**, 615 (Engl. Transl.)].
2. Al. G. Krestov, Yu. A. Lebedev, A. S. Ocheretovyj, and Yu. D. Orlov, *13th IUPAC Conf. on Chemical Thermody-*

namics, Clermont—Ferrand, France, July 17—22, 1994, 330.
3. R. Foon and K. B. Tait, *J. Chem. Soc., Faraday Trans.*, 1972, **68**, 1121.
4. D. McMillen and D. Golden, *Ann. Rev. Phys. Chem.*, 1982, **33**, 493.
5. V. P. Kolesov and T. S. Papina, *Usp. Khim.*, 1983, **52**, 754 [*Russ. Chem. Rev.*, 1983, **52** (Engl. Transl.)].
6. Yu. D. Orlov and Yu. A. Lebedev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1074 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 987 (Engl. Transl.)].
7. Yu. D. Orlov, Yu. A. Lebedev, and B. L. Korsunskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 1550 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1984, **33**, 1424 (Engl. Transl.)].
8. Yu. D. Orlov and Yu. A. Lebedev, *Zh. Fiz. Khim.*, 1991, **65**, 289 [*Russ. J. Phys. Chem.*, 1991, **65** (Engl. Transl.)].
9. W. Tsang, *J. Phys. Chem.*, 1984, **88**, 2812.
10. T. Hsieh and R. J. Hanrahan, *Int. J. Mass. Spectrom. and Ion Phys.*, 1977, **23**, 201.
11. Yu. D. Orlov and Yu. A. Lebedev, *Zh. Fiz. Khim.*, 1984, **58**, 2880 [*Russ. J. Phys. Chem.*, 1984, **58** (Engl. Transl.)].
12. E. T. Denisov, *Zh. Fiz. Khim.*, 1995, **69**, 436 [*Russ. J. Phys. Chem.*, 1995, **68** (Engl. Transl.)].
13. I. Weeks and E. Whittle, *Int. J. Chem. Kinet.*, 1983, **15**, 1329.
14. Z. B. Alfassi, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, 1973, **5**, 155.
15. D. R. Stull, E. F. Jr. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, J. Wiley and Sons, New York, 1969.
16. J. B. Pedley, R. D. Naylor, and S. P. Kirby, *Thermochemical Data of Organic Compounds*, London—New York, 1986, 792.
17. F. D. Steinkruger and F. S. Rowland, *J. Phys. Chem.*, 1981, **85**, 136.
18. M. Meot-Ner, *J. Am. Chem. Soc.*, 1982, **104**, 5.
19. L. V. Gurvich, G. V. Karachevtsev, V. N. Kondrat'ev, Yu. A. Lebedev, V. A. Medvedev, V. K. Potapov, and Yu. S. Khodeev, *Energii razryva khimicheskikh svyazei. Potentsialy ionizatsii i srodstvo k elektronu* [*Energies of Chemical Bond Cleavage. Ionization Potentials and Electron Affinity*], Nauka, Moscow, 1974 (in Russian).
20. V. V. Takhistov, *Organicheskaya mass-spektrometriya* [*Organic Mass Spectrometry*], Nauka, Leningrad, 1990 (in Russian).
21. V. P. Kolesov and M. P. Kozina, *Usp. Khim.*, 1986, **55**, 1603 [*Russ. Chem. Rev.*, 1986, **55** (Engl. Transl.)].
22. E. T. Denisov and T. G. Denisova, *Kinet. Katal.*, 1993, **34**, 199 [*Kinet. Catal.*, 1993, **34** (Engl. Transl.)].
23. E. T. Denisov, *Zh. Fiz. Khim.*, 1995, **68**, 29 [*Russ. J. Phys. Chem.*, 1995, **68** (Engl. Transl.)].

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