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The determination of enthalpies of formation of organic free radicals from bond dissociation energies
5.* Organosulfur radicals

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The formation enthalpies (ΔH_f°) of 12 organosulfur radicals ($R^\bullet$) were determined for the first time from the published values of dissociation energies of R—X bonds.

Key words: sulfur-containing free radicals, organic sulfur-containing molecules, enthalpies of formation, bond dissociation energies, phenomenological calculations, relationships "structure—property."

Many transformation of organosulfur compounds proceed *via* stages involving free radicals. That is why it is urgent to study the properties of sulfur-containing radicals, including energy parameters, the most important of which is the enthalpy of formation ΔH_f°.

The $\Delta H_f^\circ(R^\bullet)$ values are most often found from dissociation energies (D) of R—X chemical bonds in RX molecules (where X is the atom or radical)

$$D(\mathrm{R{-}X}) = \Delta H_f^\circ(\mathrm{R}^\bullet) + \Delta H_f^\circ(\mathrm{X}) - \Delta H_f^\circ(\mathrm{RX}). \qquad (1)$$

Similar calculations require data on $\Delta H_f^\circ(\mathrm{RX})$ of the starting molecules, and lacking of these data retards the replenishment of the database of $\Delta H_f^\circ(R^\bullet)$ values. In recent years we are extending the database of ΔH_f° of organic radicals $R^\bullet$, and the results of this work are presented in Refs. 1—5.

Data on ΔH_f° of sulfur-containing organic radicals are very scarce. Only 8 such radicals have been characterized by the published[6] ΔH_f° values. Seventeen corresponding values are known from Ref. 7. The ΔH_f° values found by us for 11 organosulfur radicals, which have not been described previously, are presented in Table 1.

Of 11 auxiliary ΔH_f° values of sulfur-containing molecules, 6 values were published (see Table 1) and the other values were calculated by the method of macroincrement thermochemical simulation (MTS).[17] According to the latter, the structure of the desired compound is composed of large fragments of model compounds by their "addition and subtraction," which is shown by the schematic "equation." The value of the desired property is calculated from the values of model compounds using the corresponding numerical equation similar to the simulation scheme. The value of the property of the model compound is usually written under its symbol (Eqs. (2)—(8)). The ΔH_f° values found (in kJ mol^{-1}) are given in parentheses in the left parts of the equations. In our calculations, the ΔH_f° values (in kJ mol^{-1}) of model compounds (right parts of the equations) were taken from the handbook[9] except specially indicated cases.

$$\begin{array}{ccccccc} \mathrm{Ph_2CHSPh} & = & \mathrm{Ph_2CHMe} & + & \mathrm{PhSMe} & - & \mathrm{C_2H_6} \\ (308.6) & \leftarrow & 127.5 & & 97.3\pm0.8 & & -83.8\pm0.4 \end{array} \qquad (2)$$

Table 1. ΔH_f° of organosulfur radicals (all values in kJ mol^{-1})

$R^\bullet$	$D(\mathrm{R{-}H})$	$\Delta H_f^\circ(\mathrm{RH})$	$\Delta H_f^\circ(R^\bullet)$
$\mathrm{Me_2CHS^\bullet}$	(369.9±8)[8]	(−76.2±0.7)[9]	75.7
$\mathrm{Me_3CS^\bullet}$	(370.7±8)[8]	(−109.6±0.9)[9]	43.1
$\mathrm{PhCH_2S^\bullet}$	367.4 [10]	(92.8±1.1)[9]	242.2
$\mathrm{PhC^\bullet SPh}$	344.8 [11]	308.6*	435.4
9-(PhS)$\mathrm{Fl^\bullet}$-9	312.1 [11]	339.0*	433.1(?)**
$\mathrm{MeC(S)N^\bullet H}$	381 [12]	(9.8±0.5)[14]	173
$\mathrm{PhC(S)N^\bullet H}$	377 [12]	(147.8±2.7)[15]	307
$\mathrm{H_2NC(S)N^\bullet H}$	389 [12]	(22.9±1.6)[16]	194
$\mathrm{PhSO_2C^\bullet HPh}$	(377.4±2.5)[13]	−152.4*	7.0
$\mathrm{PhSO_2C^\bullet Ph_2}$	365.3 [11]	−45.4*	101.9
9-($\mathrm{PhSO_2}$)$\mathrm{Fl^\bullet}$-9	342.7 [11]	−11.7*	113.0

Note. All values are given in kJ mol^{-1}.
* Determined in this work (see text).
** Doubtful values (see text).

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* For Part 4, see Ref. 1.

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The $\Delta H_f^\circ(\mathrm{Ph_2CHMe})$ value was calculated by the MTS method.[1]

9-(PhS)Fl = 9-MeFl + PhSMe − C_2H_6 (3)
(339.0) ← 157.9 97.3±0.8(−83.8±0.4

Symbol Fl designates fluorenyl in Eq. (3) and below. The ΔH_f° value of 9-methylfluorene was determined from the equation

9-MeFl = Fl + Me_3CH − MeCHMe (4)
(157.9) ← 187.4 −134.2±0.7 −104.7±0.5.

In turn, we recalculated $\Delta H_f^\circ(\mathrm{Fl})_{\mathrm{gas}}$ from the enthalpy of formation in the solid phase $\Delta H_f^\circ(\mathrm{Fl})_{\mathrm{mb}}$ (88.2 kJ $\mathrm{mol^{-1}}$)[18] and enthalpy of sublimation $\Delta H_{\mathrm{sub}}^\circ(\mathrm{Fl})$ (99.2 kJ $\mathrm{mol^{-1}}$)[19].

$PhSO_2CH_2Ph$ =
(152.4) ←
= $PhSO_2Me$ + $PhCH_2SO_2Me$ − $MeSO_2Me$ (5)
−253.4±3.1 −272.1±3.3 −373.1±3.0

$PhSO_2CHPh_2$ =
(−45.4) ←
= Me_2CHSO_2Ph + 2 PhMe − 2 C_2H_6 (6)
−313.8±3.1 50.4±0.6 −83.8±0.4

The $\Delta H_f^\circ(\mathrm{Me_2CHSO_2Ph})$ value was determined from Eq. (7), and ΔH_f°(9-MeFl) was found using Eq. (4).

Me_2CHSO_2Ph =
(−313.8) ←
= Me_2CHSO_2Me + $MeSO_2Ph$ − $MeSO_2Me$ (7)
−433.5±2.9 −253.4±3.1 −373.1±3.0

9-($PhSO_2$)Fl = 9-MeFl + $PhSO_2Me$ − C_2H_6 (8)
(−11.7) ← 157.9 −253.4±3.2 −83.8±0.4

All new ΔH_f° values presented in Table 1, according to the classification,[7] should be considered as preliminary by the property of uniqueness of the reference value. In the previous reports[1—4] of this series, we examined new $\Delta H_f^\circ(\mathrm{R}^\cdot)$ values on the basis of studying the quantitative correlations "structure—property." We cannot do this in this work because the structure of these radicals has many modifications and the number of radicals is relatively small. A comparative analysis of the $\Delta H_f^\circ(\mathrm{R}^\cdot)$ values in Table 1 makes it possible to introduce some remarks. The comparison of ΔH_f° of diphenylmethyl and fluoren-9-yl and their substituted derivatives (with substituents PhS and $PhSO_2$) allows the qualification of the $\Delta H_f^\circ(\text{9-(PhS)Fl}^\cdot\text{-9})$ as doubtful. This can be related to an error in determination of the reference value *D*. As can be seen in Table 1, it is much lower than other $\Delta H_f^\circ(\mathrm{R}^\cdot)$ values in the series considered. The first two $\Delta H_f^\circ(\mathrm{R}^\cdot)$ values in Table 1 were confirmed by the calculation based on the additive-group approach,[7] which gives for them 74.3 and 45.0 kJ $\mathrm{mol^{-1}}$, respectively.

References

1. Yu. D. Orlov, V. O. Lavrov, and Yu. A. Lebedev, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 923 [*Russ. Chem. Bull.*, *Int. Ed.*, 2001, **50**, 963].
2. Yu. D. Orlov, R. Kh. Zaripov, and Yu. A. Lebedev, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 643 [*Russ. Chem. Bull.*, 1998, **47**, 621 (Engl. Transl.)].
3. 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.)].
4. Yu. D. Orlov and Yu. A. Lebedev, *Izv. Akad. Nauk, Ser. Khim.*, 1999, 286 [*Russ. Chem. Bull.*, 1999, **48**, 285 (Engl. Transl.)].
5. Yu. D. Orlov, A. A. Tomilin, and Yu. A. Lebedev, *Zh. Fiz. Khim.*, 2000, **74**, 1058 [*Russ. J. Phys. Chem.*, 2000, **74** (Engl. Transl.)].
6. *Handbook of Chemistry and Physics*, CRC Press, Florida, 1995, 9; 1996, 9.
7. Yu. D. Orlov, *Doct. Sci.* (*Chem.*) *Thesis*, Tver State University, Tver, 1996 (in Russian).
8. B. K. Janousek, K. J. Reed, and J. I. Brauman, *J. Am. Chem. Soc.*, 1980, **102**, 3125.
9. J. B. Pedley, R. D. Naylor, and S. P. Kirby, *Thermochemical Data of Organic Compounds*, Chapman and Hall, London—New York, 1986.
10. E. T. Denisov, *Zh. Fiz. Khim.*, 1996, **70**, 260 [*Russ. J. Phys. Chem.*, 1996, **70** (Engl. Transl.)].
11. F. G. Bordwell, X. Zhand, and Z.-P. Chend, *J. Org. Chem.*, 1991, **56**, 3216.
12. F. G. Bordwell, J. A. Harrelson, and T.-Y. Lynch, *J. Org. Chem.*, 1990, **55**, 3337.
13. F. G. Bordwell, J.-P. Cheng, G.-Z. Ji, A. V. Satish, and X. Zhang, *J. Am. Chem. Soc.*, 1991, **113**, 9790.
14. R. Sabbah and L. A. Gomez, *Thermochim. Acta*, 1982, **52**, 285.
15. M. D. M. C. Ribeiro Da Silva, P. Souza, and G. Pilcher, *J. Chem. Thermodyn.*, 1989, **21**, 173.
16. L. A. T. Gomez and R. Sabbah, *Thermochim. Acta*, 1982, **57**, 67.
17. H. M. Rosenstock, J. Dannacher, and J. F. Liebman, *Radiat. Phys. Chem.*, 1982, **20**, 7.
18. D. R. Stull, E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, J. Wiley and Sons, New York, 1969.
19. Yu. A. Lebedev and E. A. Miroshnichenko, *Thermochemistry of Organic Substance Evaporation in Thermochemistry and Equilibria of Organic Compounds*, VCH Publ., New York, 1993, **2**, 165.

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