Physical Chemistry

Thermodynamic properties and valence—power field of thiyl radicals

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The consistent valence—force field of alkylthiyl radicals ($RS^{\cdot}$) was determined for the first time by the solution of an inverse spectral problem. The vibrational spectra of 12 linear and branched $RS^{\cdot}$ forms were calculated. The thermodynamic functions (enthalpy, entropy, heat capacity, and Gibbs free energy) were determined by methods of statistical mechanics in a temperature interval of 298—1500 K. Within the framework of the additive—group approach, the quantitative structure—property relationships were considered for the thermodynamic functions of the $RS^{\cdot}$ radicals, and the parameters of these relationships were calculated.

Key words: free radicals, alkylthiyl radicals, vibrational spectra, force constants, thermodynamic functions, structure—property relationship, additive—group approach.

Molecules containing S^{II} atoms play an important role in organic synthesis. Such compounds found wide use in agriculture, pharmaceutical industry, and polymer production; they are components of oils and coals.[1—4] Sulfur-containing compounds are significant for biochemical processes of living organisms.[3] A considerable part of chemical reactions were established[5—8] to occur through the stage of formation of free organic radicals. Therefore, recently researchers often pay attention to the determination of thermodynamic functions of radicals. Unfortunately, the number of thiyl radicals ($RS^{\cdot}$) characterized by corresponding data is very scarce, and errors of the values are often too high.[9]

The values of standard enthalpies of formation of radicals $\Delta H_f^{\circ}(RS^{\cdot})$ presented in literature are mainly calculated from the formulas

$$D(R^1S—R^2) = \Delta H_f^{\circ}(R^1S^{\cdot}) + \Delta H_f^{\circ}(R^2S^{\cdot}) - \Delta H_f^{\circ}(R^1SR^2), \quad (1)$$

$$\Delta H_f^{\circ}(R^1S^{\cdot}) = \Delta H_f^{\circ}(R^1SR^2) - \Delta H_f^{\circ}(R^{2\cdot}) + D(R^1S—R^2), \quad (2)$$

where $D(R^1S—R^2)$ are the energies of bond dissociation, and $\Delta H_f^{\circ}(R^1SR^2)$ are the standard enthalpies of formation of molecules. Errors of experimental determination of the energies of bond dissociation $D(R^1S—R^2)$ (the H

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atom most frequently acts as R^2) are 6—8 kJ mol^{-1} and in some cases reach 17 kJ mol^{-1} and more. The $\Delta H_f°(R^{\cdot})$ values are known with the same accuracy.[9] One should treat the values found by semiempirical quantum-chemical methods with care because the errors are often comparable with the magnitudes and even exceed them.

In this work, we calculated frequencies of vibrations of the RS$^{\cdot}$ radicals from the solution of the direct and inverse spectral problems in the framework of the harmonic oscillation for the valence—power field followed by the calculation of the main thermodynamic characteristics of RS$^{\cdot}$ by methods of statistical thermodynamics in the "rigid rotator—harmonic oscillator" approximation.[10] In addition, the quantitative structure—property relationships for these characteristics were studied by the additive—group approach.

Results and Discussion

Estimation of geometric parameters. The structure and some frequencies of the MeS$^{\cdot}$ radical were calculated by the *ab initio* quantum-chemical method,[11,12] which gave the bond lengths r_0(C—S) = 1.76 Å, r_0(C—H) = 1.1 Å and the S—C—H angle 111°. For all RS$^{\cdot}$ we accepted r_0(C—S) = 1.76 Å, r_0(C—H) = 1.099 Å (in CH_2) and 1.093 Å (in CH_3), r_0(C—C) = 1.543 Å; all angles considered to be tetrahedral. The MeS$^{\cdot}$ and $Me_3CS^{\cdot}$ radicals has the symmetry group C_{3v}, and the non-branched radicals belong to the point group C_s. These geometric parameters were used to find the products of the main central inertia momenta of tops of delayed internal rotation in the RS$^{\cdot}$ radicals.

Analyzing the barriers of internal rotation of the methyl, ethyl, and mercapto (—SH) groups in thiols, we noticed that the barriers of the methyl groups are close to similar barriers of alkanes, and the barrier of the mercapto group weakly depends on the functional environment. Therefore, the barriers of hindered internal rotation in RS$^{\cdot}$ were accepted the same as those in alkanes.[13]

Determination of valence—power field. The force constant of the C—S bond (K_{C-S}) in RS$^{\cdot}$ was calculated by the modified Badger formula[14—16]:

$$K_{C-S} = a_{C-S}/(r - b_{C-S})^3, \qquad (3)$$

where a and b are the constants that depend on the type of atoms forming the bond (in this case, C and S), and r is the length of this bond (Å). The parameters for the C—S bond calibrated by formula (3) using the force constants K_{C-S} of the Me_2S (dimethyl sulfide) and MeSH (methanethiol) molecules are the following: $a = 3.428 \cdot 10^6$ Å^3 cm^{-2} and $b = 0.923$ Å. The reference data, *viz.*, $K_{C-S}(Me_2S) = 5.05 \cdot 10^6$ cm^{-2} and $K_{C-S}(MeSH) = 4.8 \cdot 10^6$ cm^{-2}, were taken from previously published data.[17,18] Based on the results of calculation of the vibrational spectra of MeSH, EtSH (ethanethiol), and Me_2S, taking into account the rules of portability of force constants, we determined the force fields of thiols, dithiols, and alkyl sulfides in the ideal gas state. The corresponding force constants and calculated frequencies of vibrations for MeSH, EtSH, and Me_2S were compared with experimental ones.[17,18]

The inverse spectral problem for alkanethiols and dialkyl sulfides was solved under the condition that the averaged parameters and force constants of the "alkyl residues" R correspond to the described ones.[19] Using formula (3) and above presented a and b values, we obtained K_{C-S} in MeS$^{\cdot}$ equal to $5.8 \cdot 10^6$ cm^{-2}. According to the Fil'kenshtein—Shtenberg rule,[20,21] we recalculated (compared to thiols) the force constants of the H—C—S$^{\cdot}$ and C—C—S$^{\cdot}$ angles. The force constants of other coordinates of RS$^{\cdot}$ are taken from calculations of the corresponding RSH molecules[17,18] (Table 1).

Table 1. Force constants (K) for MeS$^{\cdot}$, MeSH, and Me_2S

Force constant*	$K \cdot 10^{-6}$/cm^{-2}		
	MeS$^{\cdot}$	MeSH	Me_2S
K_{S-H}	—	6.4	—
K_{C-S}	5.8	4.8	5.05
K_{C-H} in Me	8.2	8.2	8.2
K_{CSC}	—	—	1.8
K_{SCH}	0.95	0.94	0.85
K_{HCH} in Me	0.7	0.7	0.7
K_{CSH}	—	1.1	—
$H_{CH,CH}$ in Me	0.07	0.07	0.07
$A_{CH,SCH}$	0.35	0.35	0.35
$A_{CH,HCH}$ in Me	0.3	0.3	0.3
$A_{CS,SCH}$	0.15	0.5	0.4
$A_{CS,CSH}$	—	0.2	—
$A_{SH,CSH}$	—	0.3	—
$L_{SCH(1),SCH(2)}$	−0.025	−0.03	−0.01
$L_{SCH(1),H(1)CH(2)}$	−0.01	−0.01	−0.01
$A_{CS,SCH(i)}$	0.4	0.4	0.4
$A_{CH,CSC}$		—	0.46
$L_{C(i)SC,SCH(i)}$	—	—	0.4
$L_{CSC,SCH}$	—	—	−0.01
$H_{CS,CS}$	—	—	0.05

* H(i), C(i) are atoms lying in one plane.

Calculation of spectrum of RS$^{\cdot}$. Using the force constants (see Table 1), we calculated the spectrum of MeS$^{\cdot}$ in the ideal gas state. The calculated values agree well with the results of quantum-chemical calculation[11] (Table 2). It is of interest to compare the obtained spectrum of MeS$^{\cdot}$ with that of MeCl because the geometric structure of MeCl (in MeCl r_0(C—Cl) = 1.782 Å, r_0(C—H) = 1.103 Å, H—C—H angle is 110°20′)[22] and the weight of the Cl atom are close to those inherent in MeS$^{\cdot}$ and S. Based on the above indicated geometry and force field, we also determined the spectra of twelve other RS$^{\cdot}$ radicals. The frequencies were assigned (Tables 3 and 4) from results of the calculation of the energy distributions over natural coordinates. The fre-

Table 2. Frequencies of vibrations (ω) for MeS$^{\cdot}$ and MeCl

ω/cm^{-1}		
Calculation for MeS$^{\cdot}$		Experiment for MeCl[22]
*A**	*B***	
2999(2)	—	3041
2923	—	2966
1458(2)	—	1455
1353	1360	1355
996(2)	—	1015
768	770	732

* This work.

** See Ref. 11.

quencies of similar vibrations in the linear radicals are most close in value. In the non-linear radicals, the frequencies of the same vibrations depend on the length of the carbon chain and degree of branching. The presented tables can be used for identification of radicals from spectra.

Calculation of thermodynamic functions. Based on the above data, the thermodynamic functions ($S°(T)$, $C°_p(T)$, $H_f°(T) - H_f°(0)$, $G°(T) - H_f°(0)$) were determined by the methods of statistical thermodynamics[10] for twelve linear and branched RS$^{\cdot}$ radicals in the 298.15—1500 K interval. All parameters concern the ideal gas state. The temperature dependence of the heat capacity in this temperature interval is presented in the form

$$C°_p(T) = a + bT + cT^2 + dT^3. \quad (4)$$

The calculated values for entropy, enthalpy, and heat capacity at 298.15 K and the coefficients in Eq. (4) are presented in Table 5. When using formula (4), the errors of calculations are <1%. Similar calculations of entropy and heat capacity have previously been performed only for alkyl radicals.[24]

Structure—property relationships for thermodynamic functions. The most developed and convenient method, which determines structure—property relationships, is the method of additive—group increments, according to which molecules are simulated by a set of structural fragments, *viz.*, groups of atoms. The extensive properties of molecules are found as the sum of the corresponding contributions (increments).[25,26] This approach to the calculation of $\Delta H_f°(R^{\cdot})$ in various approximations is developed in literature.[23,27—30] The values of the $\Delta H_f°(298.15)$ increments for RS$^{\cdot}$ (see Ref. 23) are presented in Table 5. Based on the entropy and heat capacity values (coefficients in Eq. (4)) calculated by us using methods of statistical physics, we calculated the increments to $S°(298.15)$ and $C°_p(T)$ of the groups modeling the considered radicals (Tables 6 and 7).

Using the data presented in Tables 6 and 7, one can find $S°(298.15)$, $\Delta H_f°(298.15)$, and $C°_p(T)$ for the linear and branched RS$^{\cdot}$ radicals. In the calculations of the entropy using the indicated increments, the term $R\ln\sigma$

Table 3. Assignment of frequencies of vibrations (ω) for non-branched alkylthiyl radicals

Assignment*	ω/cm^{-1}				
	MeS$^{\cdot}$	EtS$^{\cdot}$	PrS$^{\cdot}$	BuS$^{\cdot}$	$C_5H_{11}S^{\cdot}$
ν(C—S)	768	742	820	818	815
ν(C—C)	—	962	890, 1029	991, 1047, 1111	898, 983, 1028, 1062
ν(C—H) in Me	2923, 2999, 2999	2894, 2969, 2970	2894, 2969, 2970	2894, 2969, 2970	2894, 2969, 2970
ν(C—H) in CH_2	—	2871, 2928	2848, 2872, 2895, 2934	2846, 2851, 2872, 2884, 2911, 2935	2845, 2848, 2852, 2872, 2879, 2898, 2919, 2935
δ(HCH) in CH_2	—	1459	1464	1450, 1461, 1466, 1472	1448, 1457, 1465, 1467, 1471
δ(HCH) in Me	1458, 1458	1459, 1466	1451, 1459, 1475	1459	1459
δ(SCH) in Me	996, 996, 1353	—	—	—	—
δ(CCH) in CH_2	—	740, 1272	693, 849, 1246, 1277, 1296	674, 766, 915, 1099, 1231, 1253, 1294, 1297, 1352	664, 724, 828, 957, 1105, 1223, 1239, 1282, 1297, 1302, 1319, 1378
δ(CCH) in Me	—	1051, 1065, 1371	1099, 1379	901, 1379	1112, 1380
δ(SCH) in CH_2	—	1394	1085, 1411	1414	1414
δ(CCC)	—	—	248, 362	161, 329, 393	118, 257, 334, 442
δ(SCC)	—	344	248	161, 393	257

* Designations: ν is stretching vibration, and δ is deformational vibration.

Table 4. Assignment of frequencies of vibrations (ω) for non-linear radicals

Assignment*	ω/cm^{-1}		
	$Me_2C_3H_5S^{\cdot}$	$Me_3C_3H_4S^{\cdot}$	$Me_2C_4H_7S^{\cdot}$
ν(C—S)	836	836	833
ν(C—C)	783, 955, 970	726, 913, 915, 1027, 1274	773, 950, 981, 1020
ν(C—H) in Me	2894(2), 2967, 2969(2), 2971	2894(3), 2967, 2968(2), 2969, 2970(2)	2894, 2894, 2967, 2969, 2969, 2971
ν(C—H) in CH_2	2847, 2872, 2896	2848, 2872, 2896, 2934	2845, 2851, 2872, 2885, 2912, 2935
ν(C—H) in CH	2884	—	2884
δ(HCH) in CH_2	1463, 1466	1462, 1465	1443, 1463, 1468
δ(HCH) in Me	1455, 1460, 1465, 1473	1456, 1457(2), 1467, 1468, 1477	1455, 1461, 1464, 1472
δ(CCH) in CH	1351, 1363	—	1351
δ(CCH) in CH_2	718, 1114, 1223, 1265, 1294	716, 1143, 1206, 1282, 1295, 1310	681, 810, 1013, 1116, 1196, 1227, 1290, 1298, 1328, 1363
δ(CCH) in Me	916, 960, 974, 1126, 1198, 1379(2)	939, 973, 978, 989, 1004, 1381(3)	924, 962, 1139, 1200, 1379, 1379
δ(SCH) in CH_2	1414	1413	1412
δ(CCC)	154, 353, 383, 514	144, 349, 355, 404, 426, 467	108, 253, 365, 380, 539
δ(SCC)	280	254	333

	$Me_2CHS^{\cdot}$	$Me_3CS^{\cdot}$	$EtMeCHS^{\cdot}$	$EtMe_2CS^{\cdot}$
ν(C—S)	693	624	741	842
ν(C—C)	878, 1113	624, 839, 1273(2)	863, 1017, 1141	653, 1005, 1287
ν(C—H) in Me	2893, 2894, 2967, 2969(2), 2971	2894(3), 2967, 2968(2), 2970, 2971(2)	2894(2), 2969(3), 2970	2894(3), 2968, 2969(3), 2970(2)
ν(C—H) in CH_2	—	—	— 2849, 2891	2848, 2900
ν(C—H) in CH	2900	—	2909	—
δ(HCH) in CH_2	—	—	1476	1477
δ(HCH) in Me	1455, 1460, 1466, 1476	1454(2), 1456, 1469(2), 1480	1454, 1459, 1462, 1466	1455, 1456, 1459, 1462, 1466, 1475
δ(CCH) in CH	1359	—	1404	—
δ(CCH) in CH_2	—	—	785, 1287	783, 1231, 1256, 1319, 1355
δ(CCH) in Me	934, 951, 1082, 1159, 1380, 1394	922(2), 978, 1025(2), 1313, 1379(3)	960, 983, 1173, 1371, 1379	918, 940, 1005, 1049, 1062, 1379(2), 1380
δ(SCH) in CH	1370, 1082	—	1081	
δ(CCC)	405	388(2)	213, 400	192, 363, 376, 407
δ(SCC)	330, 338	317(2), 339	323, 367	312, 313

* For designations, see Table 3.

Table 5. Values of $\Delta H_f°(298.15)$, $S°(298.15)$, $C_p°(298.15)$, and coefficients in Eq. (4) for the 298.15—1500 K interval

Radical	$\Delta H_f°(298.15)$ /kJ mol^{-1}	$S°(298.15)$	$C_p°(298.15)$	a	$b \cdot 10^3$ /J mol^{-1} K^{-2}	$-c \cdot 10^5$ /J mol^{-1} K^{-3}	$d \cdot 10^9$ /J mol^{-1} K^{-4}
		J mol^{-1} K^{-1}					
$MeS^{\cdot}$	128.0±5.0 [12]	238.73	40.65	11.93	111	5.36	9.98
$EtS^{\cdot}$	106.7±5.0 [12]	280.15	63.09	9.655	211	11.2	23.3
$PrS^{\cdot}$	85.8±8.4 [12]	321.53	85.46	6.227	315	17.6	38.3
$BuS^{\cdot}$	—	364.19	107.95	3.030	419	23.9	53.0
$C_5H_{11}S^{\cdot}$	—	407.75	130.42	−0.125	523	30.2	67.7
$Me_2CHS^{\cdot}$	71.6±8.4 [23]	307.88	88.19	9.630	313	17.7	39.2
$Me_3CS^{\cdot}$	43.5±8.4 [23]	320.11	114.35	6.407	432	25.4	57.3
$EtMeCHS^{\cdot}$	—	351.16	110.97	10.040	402	22.5	49.4
$EtMe_2CS^{\cdot}$	—	377.29	138.66	17.230	485	27.4	60.7
$Me_2C_3H_5S^{\cdot}$	—	407.75	132.25	0.376	530	31.3	71.5
$Me_3C_3H_4S^{\cdot}$	—	409.47	157.96	−6.781	665	40.4	93.7
$Me_2C_4H_7S^{\cdot}$	—	434.53	154.50	−5.442	645	38.6	89.4

Table 6. Increments of various groups to $S^\circ(298.15)$ and $\Delta H_f^\circ(298.15)$

Group	$S^\circ(298.15)$ /J mol^{-1} K^{-1}	$\Delta H_f^\circ(298.15)$* /kJ mol^{-1}	Group	$S^\circ(298.15)$ /J mol^{-1} K^{-1}	$\Delta H_f^\circ(298.15)$* /kJ mol^{-1}
Me—(X) (X = C, $S^\cdot$)	71.43	−41.04	(C)—$S^\cdot$	176.43	169.79
(C)—CH_2—(C)	43.11	−21.76	(C)—CH_2—($S^\cdot$)	40.01	−21.76**
$(C)_2$—CH—(C)	6.99	−13.39	$(C)_2$—CH—($S^\cdot$)	6.94	−13.39**
$(C)_3$—C—(C)	−27.85	−1.67	$(C)_3$—C—($S^\cdot$)	−31.61	−1.67**

* See Ref. 23.

** In the first approximation, they are accepted equal to similar increments of alkyls.[23]

Table 7. Increments of various groups to $C_p^\circ(T)$ (see Eq. (4))

Group	a /J mol^{-1} K^{-1}	$b \cdot 10^3$ /J mol^{-1} K^{-2}	$c \cdot 10^5$ /J mol^{-1} K^{-3}	$d \cdot 10^9$ /J mol^{-1} K^{-4}
(C)—$S^\cdot$	13.56	−40.59	4.04	−12.23
Me—(X) (X = C, $S^\cdot$)	−1.63	151.59	−9.4	22.21
(C)—CH_2—($S^\cdot$)	−4.11	106.35	−6.43	14.89
(C)—CH_2—(C)	−2.08	99.77	−5.95	13.8
$(C)_2$—CH—($S^\cdot$)	0.57	45.02	−2.36	5.21
$(C)_3$—C—(C)	−9.27	44.7	−3.86	10.6
$(C)_2$—CH—(C)	−5.6	68.91	−4.83	12.66
$(C)_3$—C—($S^\cdot$)	4.19	−5.57	0.73	−2.31

should be subtracted from the obtained value, where R is the universal gas constant; $\sigma = \rho\sigma_{mol}\sigma_1\sigma_2$ ..., σ_{mol} and σ_i are the indices (numbers) of symmetry of the radical and ith top of internal rotation, respectively; and ρ is the weight of the ground electronic state (usually for radicals $\rho = 2$). The Gibbs energy $\Delta G_f^\circ(T)$ is determined using the following formulas:

$$\Delta G_f^\circ(T) = \Delta H_f^\circ(T) - TS^\circ(T), \quad (5)$$

$$\Delta H_f^\circ(T) = \Delta H_f^\circ(298.15) + \int_{298.15}^{T} C_p(T)\mathrm{d}T, \quad (6)$$

$$S^\circ(T) = S^\circ(298.15) + \int_{298.15}^{T} [C_p(T)/T]\mathrm{d}T. \quad (7)$$

The error for determination of $C_p^\circ(T)$ from the data in Table 7 was maximum for $Me_3CS^\cdot$. In the whole 298—1500 K interval, the relative error for heat capacity is at most 1%.

Thus, in this work, the power field was proposed for the first time for the $RS^\cdot$ radicals. The frequencies of vibrations for twelve radicals were calculated and assigned. The entropy, enthalpy, and heat capacities for these radicals were determined. In the framework of the additive—group method, the increments from the groups to the $\Delta H_f^\circ(298)$ and $S^\circ(298)$ values and to the coefficients in Eq. (4) were found, which allow one to calculate the thermodynamic functions for any alkylthiyl $RS^\cdot$ radical in the 298—1500 K temperature interval.

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