Russian Chemical Bulletin, International Edition, Vol. 50, No. 9, pp. 1563—1569, September, 2001

Thermodynamic properties and valence-force field of alkanethiols and dialkyl sulfides

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The consistent valence-force field of alkanethiols (AlkSH), dialkyl sulfides (AlkSAlk′), and alkanedithiols (HS*R*SH, *R* is alkylene) was determined for the first time by the solution of an inverse spectral problem. The vibrational spectra of 40 linear and branched molecules AlkSH, *R*S*R*′, and HS*R*SH were calculated. Their thermodynamic functions (enthalpy, entropy, thermal capacity, and free Gibbs energy) were determined by methods of statistical mechanics in the 298—1500 K temperature interval. Within the framework of the additive-group approach, the quantitative relationships "structure—property" were considered for the thermodynamic functions of AlkSH, AlkSAlk′, and HS*R*SH, and the parameters of the relationships were calculated. The results of calculations and experimental data were compared.

Key words: alkanethiols, dialkyl sulfides, vibrational spectra, force constants, thermodynamic functions, calculation of properties, relationships "structure—property," additive-group approach.

Virtually all petroleum deposits of our country contain great amounts of sulfur compounds. Therefore, petroleum refinement and obtaining of the most valuable raw material, organosulfur compounds, are among the most important problems of petrochemistry. In recent time, the theory of reactions of such compounds has been developed in detail,[1—7] however, much less attention is given to the estimation of their thermodynamic parameters. At the same time, knowing these characteristics facilitates the development and improvement of the corresponding technologies.

The most thermodynamic parameters presented[8—10] for AlkSH and AlkSAlk′ were obtained by Scott and McCullough. They calculated the thermodynamic functions of these molecules using the experimental values and those calculated by statistical thermodynamics methods using spectral data and temperature plots of thermal capacities of several first molecules of the homological series indicated (eight alkanethiols, four alkanesulfides, and two alkanedisulfides). Then their increments (contributions of the CH_2 and Me groups) were found in the framework of the additive-group model[11] and characteristics of other HAlkSH and AlkSAlk′ molecules with the normal structure were obtained by the addition of the increment of CH_2 to the corresponding parameter of the preceding molecule of the series.[8,10]

Note that standard enthalpies of formation of molecules from simple substances $\Delta H_f°(298)$ were obtained under the assumption of S_2 formation from gaseous sulfur and later were recalculated by other researchers relatively to orthorhombic sulfur. Therefore, the enthalpies presented in reference books differ within 1 kJ mol^{-1}.[10,12—14] Thermodynamic parameters for branched molecules are very scarce in literature (these are mainly $\Delta H_f°(298)$), and all of them refer to C_3—C_5 molecules and 298 K.[12,13,15] For HS*R*SH (*R* is alkylene) only four $\Delta H_f°(298)$ values were published,[10,12—14] and parameters for polythiols are unknown at all.

This work is aimed, first, at calculating the main thermodynamic characteristics (enthalpy, entropy, thermal capacity, and free Gibbs energy) for several key molecules AlkSH, HS*R*SH, and AlkSAlk′ in the 298—1500 K temperature interval and, second, at determining the reference parameters and developing the calculation methods, which allow the establishment of these characteristics for any molecules of the series indicated. With this purpose, we used the methods of calculation of vibrations of molecules in the harmonic approximation for the valence-force method and the calculation apparatus of statistical mechanics of molecules. Parameters of the geometric structure, force fields, and internal rotations of molecules are the refer-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1487—1493, September, 2001.

1066-5285/01/5009-1563 $25.00 © 2001 Plenum Publishing Corporation

ence data for these methods. The quantitative "structure—property" relationships were searched for in the framework of the additive-group approach.

Estimation of geometric parameters

Published data on the geometry of thiols AlkSH and sulfides AlkSAlk′ differ insignificantly. The following consistent values were accepted for the mercapto group (—SH) in в AlkSH and HS*R*SH: *r*(C—S) = 1.817 Å, *r*(S—H) = 1.329 Å, angle C—S—H = 96°[16]; in AlkSAlk′ *r*(C—S) = 1.802 Å, angle C—S—C = 98°52′.[17] The averaged parameters of the "alkyl tail" are standard: all angles are equal to tetrahedral of 109°28′16″, *r*(C—H) = 1.093 Å in (Me), *r*(C—H) = 1.099 Å in (CH_2), *r*(C—H) = 1.099 Å in (CH) and *r*(C—C) = 1.543 Å, which corresponds to the geometry of alkanes accepted in literature.[18] Nonbranched thiols AlkSH have C_s symmetry (the symmetry plane coincides with the plane of the CSH angle, the molecule is symmetric relatively to the plane).[19,20] Molecules of dimethyl sulfide Me_2S and other alkanesulfides Alk_2S belong to the symmetry group C_{2v} (they have the symmetry axis of the second order and two symmetry planes), and molecules of nonbranched dialkyl sulfides AlkSAlk′ are attributed to the C_s group. Using the accepted parameters, the main central moments of inertia, their products ($I_AI_BI_C$), and reduced moments of inertia (I_{np}) of tops of delayed internal rotation of the molecules considered.

Calculation of vibrational frequencies

The reliable frequencies and assignments of the vibrational spectra of methanethiol (MeSH), ethanethiol (EtSH), and dimethyl sulfide (Me_2S) were obtained.[19] In addition, some frequencies were assigned by the groups of vibrations of the first terms of the homological series of alkane-1-thiols, alkane-2-thiols, dialkyl sulfides, and dialkyl disulfides.[21] Based on these spectra of MeSH, EtSH, and Me_2S,[19] we solved the inverse spectral problem for these classes of molecules. When solving it, the condition was imposed: the force constants of "alkyl residues" should correspond to those of alkanes recommended in the previous work.[18] The consistent force field was found for the first time for AlkSH and AlkSAlk′. It allowed the calculation of the spectra of the molecules with both normal and branched structures.

The found values (Table 1) of the force constants were used for the determination of the vibrational frequencies of other AlkSH, AlkSAlk′, and HS*R*SH compounds. All calculations were performed using the original program, which allows the calculation of the primal and inverse problems and the determination of the geometric and thermodynamic parameters of molecules. The force field obtained reproduce satisfactorily the vibrational spectra (Table 2). This is especially significant for the low-frequency region because provides a rather reliable estimation of the vibrational contribution to the thermodynamic functions.[22] Note that the frequencies obtained supplement substantially the available experimental values.

The vibrational frequencies of MeSH, EtSH, and Me_2S calculated by us are compared with the experimental values in Table 2. We cannot present here all found frequencies and their assignments because the number of calculated molecules is great (40).

The calculation showed that for AlkSH in the state of the ideal gas ~95% energy of the stretching vibration

Table 1. Force constants of molecules of alkanethiols, alkanedithiols, and dialkyl sulfides (10^6 cm^{-2})

Force constants	MeSH	EtSH	Me_2S
K(S—H)	6.4	6.4	—
K(C—S)	4.8	4.7	5.05
K(C—H) in Me	8.2	8.03	8.2
K(C—H) in CH_2	—	7.8	—
K(C—C)	—	6.6	—
K(CSC)	—	—	1.8
K(SCH)	0.94	0.94	0.85
K(HCH) in Me	0.7	0.71	0.7
K(HCH) in CH_2	—	0.7	—
K(SCC)	—	1.5	—
K(CSH)	1.1	1.12	—
K(CCH) in CH_2	—	0.93	—
K(CCH) in Me	—	0.92	—
H(CH, CH) in Me	0.07	0.06	0.07
H(CH,CH) in CH_2	—	0.01	—
A(CH, SCH)	0.35	0.35	0.35
A(CH,HCH) in Me	0.3	0.3	0.3
L(CSC, SCH)	—	—	−0.01
A(CH,HCH) in CH_2	—	0.3	—
A (CH, CCH)	—	0.46	—
A(CS, SCH)	0.5	0.5	0.4
A(CS, CSH)	0.2	0.2	—
A(CC, CCS)	—	0.3	—
A(CC, CCH)	—	0.2	—
A(SH, CSH)	0.3	0.3	—
A(CS, CCS)	—	0.45	—
L(SCC_i,CCH_i) in Me	—	0.2	—
L(CSH, SCH)	—	−0.02	—
L(CSH_i, SCC_i)	—	0.18	—
L(SCH_1, SCH_2)	−0.03	−0.03	−0.01
L(SCH_1, H_1CH_2)	−0.01	−0.01	−0.01
L(CCH_1, CCH_2)	—	−0.025	—
L(CCH_1, H_1CH_2)	—	−0.05	—
A(CS, SCH_i)	0.4	—	0.4
A(CH, CSC)	—	—	0.46
L(C_iSC, SCH_i)	—	—	0.4

Note. H_i, C_i are atoms lying in one plane.

Table 2. Experimental and calculated frequencies (cm^{-1}) of vibrations of methanethiol, ethanethiol, and dimethyl sulfide

Methanethiol			Ethanethiol			Dimethyl sulfide				
IR[19,24]	Raman*[19,42]	Calculation	IR[19]	Raman*[19,42]	Calculation	Raman*[9,42]	IR*[9,17]	Raman*[19]	IR[19]	Calculation
3000	2999	2996	3050	2966	2970	2984 **	—	2988	2998	2999
3000	2999	2995	—	2966	2969	2980	—	2988	2998	2996
—	2931	2930	—	2930	2928	—	—	—	2970	2996
2597	2572	2572	—	2872	2894	2952	—	2952	—	2996
1475	—	1442	2800	2872	2871	—	—	—	2930	2928
1430	1428	1441	2580	2570	2572	2911	2924	2914	2930	2928
1335	1319	1313	1453	1448	1463	2852	—	—	—	—
1074	1057	1067	1453	1448	1460	2844 **	—	—	—	—
976	—	982	1453	1448	1459	2832	—	—	—	—
803	805	805	1385	1374	1377	2734	—	—	—	—
708	703	701	~1309		1314	—	1460	1436	1444	1429
			1269	1265	1269	—	—	1436	1444	1429
			1092	1092	1091	1440	1441	1420	1439	1428
				1049	1047	1423	1420	1420	—	1425
			978	968	979	1335 **	1334	1326	1331 *	1327
			870	870	869	1328	1309	—	1315	1325
			745	737	740		1274	—	—	—
			660	657	655	1234	1242	—	—	—
				332	334		1074	—	—	—
						1043	1039	—	—	1031
							1028	—	—	—
							~1000	—	—	—
							976	—	—	—
						972 **	972	—	973	944
						919	917	919	—	939
							906	—	903	928
							803	—		—
						742	741	740	743 *	737
							708	—	—	—
						691	691	691	~695	692
						480	—	—	—	—
						283	282	284	282 *	280
						—	—	—	182	—

* In the liquid phase.

** Absent from literature.[42]

of the S—H bond falls per frequency of 2572 cm^{-1} assigned to this vibration and this frequency must be constant in the absence of the molecular interaction. Therefore, the scatter (2566—2576 cm^{-1}) of the corresponding experimental values obtained for the condensed state characterizes intermolecular interactions of AlkSH in the liquid and solid states, changes in the geometry of the molecules and their electron densities, and the strength of hydrogen bonds of the mercapto group.[23]

It seems impossible to eliminate the discrepancy between the calculated (944 and 928 cm^{-1}) and experimental (973 and 903 cm^{-1}) frequencies of the deformational vibrations of the SCH angle (see Table 2) without a considerable increase in the number of force constants because the derivatives of frequencies with respect to the force constants of these vibrations are the same in sign and approximately equal in value. This discrepancy can be related to the resonance of these vibrations.

Calculation of thermodynamic functions

The thermodynamic functions ($S°(T)$, $C°_p(T)$, $H°(T) - H°(0)$, $G°(T) - H°(0)$) of twenty thiols AlkSH, ten sulfides AlkSAlk′, and ten dithiols HS*R*SH in the state of the ideal gas in the 298.15—1500 K temperature region were calculated by the formulas of statistical mechanics[43] in the approximation "rigid rotator—harmonic oscillator" using the molecular constants and spectral parameters estimated in this work. The barriers of the hindered internal rotation of the —SH group in AlkSH and HS*R*SH were taken from Refs. 10 and 24, the barrier of rotation about the C—S bond in AlkSAlk′ was also published,[10,17,25] and the barriers for alkyl groups were accepted to be equal to those for alkanes.[26,27] Similar regularities based on the principle of transfer of force constants in series of related organic compounds are widely used for the estimation of thermodynamic functions, whose experimental values are unknown.[28—32] The calculated values are presented in

Table 3, and in Table 4 some $S°(298)$ и $C_p^\circ(298)$ values calculated by us are compared with the corresponding experimental values.

"Structure—property" relationships for thermodynamic functions

Phenomenological methods based on the "structure—property" interrelation are a rather simple and efficient tool for the estimation of thermodynamic values of organic molecules.[28,33–35] Among them, the additive-group model can be considered most developed.[11] Based on the obtained values, we calculated the parameters of this model. These parameters are increments (contributions) of functional groups of atoms to the value of the property. Remind that a group, by definition,[11] is a multivalent atom with its monovalent substituents. Increments of similar groups can differ depending on their nearest environment.

Tables 5—7 contain the set of groups from which the AlkSH and AlkSAlk′ molecules were simulated and their increments (contributions to $H_f°$, $S°$, and C_p°) found by the least-squares method. As in the calculations of the force constants, the increments of the groups modeling "alkyl residues" were assumed the same as those for alkanes; they are taken from the previously published works.[27,33] For the groups containing bivalent sulfur, we also refined the contributions to $\Delta H_f°$, which are also presented in literature.[33] This increased the accuracy of calculations of $\Delta H_f°$. The temperature de-

Table 3. Thermodynamic functions $\Delta H_f°(298)$ (kJ mol^{-1}), $S_p^\circ(298)$ (J (mol K)$^{-1}$), and $C_p^\circ(298)$ (J (mol K)$^{-1}$), and coefficients in Eq. (1) at 298—1500 K (all values are referred to the state of ideal gas)

Compound	$\Delta H_f°(298)$*	$S_p^\circ(298)$	$C_p^\circ(298)$	a	$b \cdot 10^{-3}$	$c \cdot 10^{-5}$	$d \cdot 10^{-9}$
Methanethiol	−22.9	254.72	51.11	20.12	117	−5.15	8.5
Ethanethiol	−46.3	296.10	73.50	17.85	217	−11.0	21.9
Propanethiol	−67.9	337.68	95.82	14.11	322	−17.5	37.5
Propane-2-thiol	−76.2	323.69	98.61	17.86	319	−17.5	38.0
2-Methylpropane-2-thiol	−109.6	335.794	125.051	16.20	433	−24.7	54.1
2,2-Dimethylpropane-1-thiol	−129.0	377.556	146.529	8.67	554	−33.2	77.2
2-Methylpropane-1-thiol	−97.3	365.068	120.481	12.14	429	−24.3	54.2
Dimethyl sulfide	−37.5	285.08	75.74	25.05	196	−9.42	17.9
Butanethiol	−88.1	379.80	118.11	9.73	431	−24.3	53.9
Pentane-1-thiol	−110.1	423.07	140.442	5.76	538	−31.0	69.8
Hexane-1-thiol	−129.9	467.15	162.78	1.79	645	−37.6	85.7
3,3-Dimethylpropanethiol	−115.1**	407.063	142.574	8.19	538	−31.4	71.5
Methylpropane-1-thiol	−94.7**	367.085	121.304	14.11	427	−24.4	54.8
Methyl ethyl sulfide	−59.6	332.12	97.72	22.53	294	−15.0	30.4
Methyl propyl sulfide	−82.3	374.924	120.036	18.51	401	−21.7	46.3
Diethyl sulfide	−83.6	368.49	119.74	20.09	391	−20.6	42.9
Ethyl propyl sulfide	−104.7	416.337	142.053	16.07	498	−27.3	58.8
Dipropyl sulfide	−125.3	453.864	164.366	12.06	605	−33.9	74.7
Isopropyl ethyl sulfide	−105.5**	415.873	141.727	15.47	500	−27.4	59.2
Ethyl isobutyl sulfide	−132.0**	446.602	167.617	16.43	602	−34.1	75.8
Diisobutyl sulfide	−179.5	515.75	215.46	12.78	813	−47.5	109.0
Butane-1,4-dithiol	−50.4	438.563	137.905	24.02	458	−26.9	61.8
Pentane-1,5-dithiol	−71.0	483.17	160.34	20.41	564	−33.5	77.3
Hexane-1,6-dithiol	−91.3**	529.01	182.78	16.79	670	−40.0	92.9
Butane-1-thiol	−97.0**	366.74	121.33	17.74	410	−22.6	49.2
Butane-2-thiol	−96.9	366.78	121.51	18.27	409	−22.5	48.8
2-Methylbutane-2-thiol	−126.4**	393.08	149.01	25.87	490	−27.1	59.4
2-Methylpentane-2-thiol	−146.8**	420.27	170.27	12.11	632	−36.4	81.1
2,2-Dimethylbutane-1-thiol	−149.4**	432.15	169.51	5.49	658	−38.7	87.1
3,3-Dimethylbutane-1-thiol	−149.4**	425.55	169.61	5.42	661	−39.4	90.1
4-Methylpentane-1-thiol	−135.5**	450.67	165.96	6.64	639	−37.3	84.4
4,4-Dimethylpentane-1-thiol	−155.9**	472.27	192.06	2.22	765	−45.7	105.0
2-Methylheptane-2,7-dithiol	−149.5**	588.03	236.02	21.39	865	−51.6	118.0
2,4-Dimethylhexane-1,6-dithiol	−144.2**	593.68	232.46	12.91	891	−54.0	126.0
Heptane-2,7-dithiol	−120.2**	564.60	209.55	22.03	756	−45.1	105.0
2,2-Dimethylhexane-1,6-dithiol	−152.1**	582.80	236.88	24.33	862	−52.4	124.0
2-Methylhexane-1,6-dithiol	−117.8**	561.11	210.62	22.30	760	−45.4	105.0
3,3-Dimethylhexane-1,6-dithiol	−152.1**	587.82	235.34	14.66	891	−54.0	125.0
3-Methylhexane-1,6-dithiol	−117.8**	556.78	209.69	20.55	763	−45.7	106.0
Methyl isobutyl sulfide	−107.4**	400.07	144.34	15.81	513	−28.9	64.1

* According to data in Ref. 13.

** Found from increments (present work).

Table 4. Experimental[9,10,12,15,29,36] and calculated thermodynamic parameters ($S°$/J (mol K)$^{-1}$, $C_p°$/J (mol K)$^{-1}$) for alkanethiols and dialkyl sulfides at 298.15 K

Molecule	$S°$/J (mol K)$^{-1}$			$C_p°$/J (mol K)$^{-1}$		
	I	II	Experiment	I	II	Experiment
Methanethiol	254.72	258.99	254.64 254.97 255.06	51.11	51.19	50.25 50.42 50.71
Ethanethiol	296.10	305.01	296.10	73.50	73.87	72.68
Propane-1-thiol	337.68	344.34	336.39	95.82	96.77	94.77
Propane-2-thiol	323.69	329.03	324.30	98.61	97.95	95.98
Butane-2-thiol	366.78	368.36	366.73 366.81	121.51	120.85	119.29 120.96
2-Methylpropane-2-thiol	335.79	341.19	338.03	125.05	124.70	120.96
2-Methylpropane-2-thiol	365.07	371.18	362.88	120.48	118.86	118.32
Dimethyl sulfide	285.08	282.29	285.56 285.85	75.74	75.43	74.10
Methyl ethyl sulfide	332.12	334.07	333.13	97.72	98.11	95.10
Diethyl sulfide	368.49	374.33	368.02	119.74	120.79	117.03

Note. The maximum error (to 3%) is referred to C_1—C_3 molecules, then the error decreases to less than 1%. I, calculation by the statistical mechanics method; II, calculation by the increment method.

pendence of the thermal capacity in the 298.15—1500 K region was presented in the form

$$C_p°(T) = a + bT + cT^2 + dT^3. \qquad (1)$$

The cubic temperature dependence (1) of the thermal capacity is very rarely met in literature, and at most 5—6 quadratic dependences were found for the molecules considered.[36] Our studies of forty molecules showed that in the studied temperature region only cubic function (1) gave an error <1%, and the quadratic function gives an error >3%, and the function

$$C_p°(T) = a + bT + cT^{-2} \qquad (2)$$

results in an error of at least 10%. It is important to take into account the cubic term in Eq. (1) (despite the smallness of coefficient d) in calculation in the high-temperature region. The increments were found for each coefficient in Eq. (1) for the temperature region indicated (see Table 6).

Table 5. Increments of the enthalpy of formation ($\Delta H_f°(298)$/J mol^{-1})

Group	$\Delta H_f°$ /kJ mol^{-1}	$S°$ /J (mol K)$^{-1}$
(C)—SH	19.75	141.34
$(C)_2$—CH—(S)	−10.46	−47.6
—S—	49.99	52.76
Me—(X) (X = C, S)	−42.96	126.78*
$(C)_3$—C—(C)	4.73	−146.44*
$(C)_3$—C—(S)	3.19	−143.95
(C)—CH_2—(S)	−24.59	46.02
$(C)_2$—CH—(C)	−3.9	−51.46*
(C)—CH_2—(C)	−20.41	39.33*

* According to data in Ref. 27.

In calculations of the entropy from the corresponding increments, the term $RLn\sigma$ should be subtracted from the obtained value, where $\sigma = \rho\sigma_{mol}\sigma_1\sigma_2...$; σ_{mol} is the index (number) of symmetry of the molecules and σ_i is that of the ith internal rotation, and ρ is the weight of the ground electron state (usually $\rho = 1$). The calculated and experimental values of $C°_p(298)$, $S°(298)$, and $\Delta H_f°(298)$ are compared in Tables 4 and 7. The $\Delta G_f°(T)$ value is determined from Eq. (3) taking into account (4) and (5):

$$\Delta G_f°(T) = \Delta H_f°(T) - TS°(T), \qquad (3)$$

at

$$\Delta H_f°(T) = \Delta H_f°(298.15) + \int_{298.15}^{T} C_p(T)\mathrm{d}T\,, \qquad (4)$$

$$S°(T) = S(298.15) + \int_{298.15}^{T} \frac{C_p\mathrm{d}T}{T}\,. \qquad (5)$$

Table 6. Increments of the entropy $S°(298)$/J (mol K)$^{-1}$

Group	a	$b \cdot 10^{-3}$	$c \cdot 10^{-5}$	$d \cdot 10^{-9}$
(C)—SH	18.67	22.52	−1.17	1.96
Me—(X) (X = C, S)*	−0.418	102.17	−4.94	9.46
(C)—CH_2—(S)	−2.72	102.31	−6.17	14.26
(C)—CH_2—(C)*	−1.05	95.73	−5.55	12.43
$(C)_2$—CH—(S)	−1.38	93.63	−6.96	19.04
$(C)_3$—C—(C)*	−17.07	159.49	−15.07	44.73
$(C)_2$—CH—(C)*	−7.2	111.04	−8.39	23.53
$(C)_3$—C—(S)	−0.78	99.02	−8.65	24.37
—S—	25.97	−9.66	0.66	−1.84

Note. The values of a/J (mol K)$^{-1}$, b/J (mol K^2)$^{-1}$, c/J (mol K^3)$^{-1}$, d/J (mol K^4)$^{-1}$ are given.

* According to data in Ref. 27.

Table 7. Comparison of experimental and calculated by increments values of $\Delta H_f^\circ(298)$/kJ mol^{-1}

Molecule	$\Delta H_f^\circ(298)$		δ*
	Experiment[13]	Calculation	
Methanethiol	−22.9	−23.21	0.31
Ethanethiol	−46.3	−47.80	1.50
Propane-1-thiol	−67.9	−68.21	0.31
Propane-2-thiol	−76.2	−76.63	0.43
2-Methylpropane-1-thiol	−97.3	−94.66	−2.64
Dimethyl sulfide	−37.5	−35.93	−1.57
Ethyl methyl sulfide	−59.6	−60.52	0.92
Butane-1-thiol	−88.1	−88.62	0.52
Butane-2-thiol	−96.9	−97.04	0.14
Methyl propyl sulfide	−82.3	−80.93	−1.37
Diethyl sulfide	−83.6	−85.11	1.51
Pentane-1-thiol	−110.1	−109.03	−1.07
2-Methylbutane-2-thiol	−127.1	−126.35	−0.75
Methyl butyl sulfide	−102.2	−101.34	−0.86
Ethyl propyl sulfide	−104.7	−105.52	0.82
3-Methylbutane-1-thiol	−114.9	−115.07	0.17
2,2-Dimethylpropane-1-thiol	−129.0	−128.99	−0.01
Ethane-1,2-dithiol	−9.7	−9.68	−0.02
Butane-1,4-dithiol	−50.4	−50.50	0.10
Pentane-1,5-dithiol	−71.0	−70.91	−0.09

* $\delta = \Delta H_f^\circ(298)_{\mathrm{exp}} - \Delta H_f^\circ(298)_{\mathrm{calc}}$.

The presented parameters are appropriate for calculations of ΔH_f° of alkanepolythiols only in the case where the contributions of nonvalent interactions of the SH groups to ΔH_f° of the indicated molecules are negligible. These contributions can quantitatively be estimated using the method of macroincrement simulation (macroincrementing).[37] According to the latter, the increments to ΔH_f° of the SH groups in positions 1, 2, 1, 3, *etc.* (designated as $\Delta_{1,2}$(SH—SH), $\Delta_{1,3}$(SH—SH), *etc.*) can be determined from the following expressions:

$$\underset{-0.9\pm1.3}{\Delta_{1,2}(\mathrm{SH{-}SH})} \underset{\leftarrow}{=} \underset{-9.7\pm1.1}{\{\mathrm{SH(CH_2)_2SH}\}} - \{2\,\underset{-46.3\pm0.6}{\mathrm{MeCH_2SH}} - \underset{-83.8\pm0.4}{\mathrm{MeMe}}\}, \tag{6}$$

$$\underset{0.7\pm1.6}{\Delta_{1,3}(\mathrm{SH{-}SH})} \underset{\leftarrow}{=} \underset{-29.7\pm1.3}{\{\mathrm{SH(CH_2)_3SH}\}} - \{\underset{-46.3\pm0.6}{\mathrm{MeCH_2SH}} + \underset{-67.9\pm0.7}{\mathrm{Me(CH_2)_2SH}} - \underset{-83.8\pm0.4}{\mathrm{MeMe}}\}, \tag{7}$$

$$\underset{1.0\pm1.9}{\Delta_{1,4}(\mathrm{SH{-}SH})} \underset{\leftarrow}{=} \underset{-50.4\pm1.8}{\{\mathrm{SH(CH_2)_4SH}\}} - \{2\,\underset{-67.9\pm0.7}{\mathrm{Me(CH_2)_2SH}} - \underset{-83.8\pm0.4}{\mathrm{MeMe}}\}. \tag{8}$$

The right parts of the upper rows of Eqs. (6)—(8) contain in braces the molecules with the interaction considered, and the second braces contain their models built from the corresponding molecules in such a way that this interaction is ignored *a priori*. Then the difference between the ΔH_f° values of a real molecule and its model is equal to the desired contribution. The contributions calculated from the experimental values[13] of ΔH_f° for the corresponding molecules are presented in the left parts of the second rows of Eqs. (6)—(8). The errors of these values were calculated as root-mean-square errors of ΔH_f° of the model compounds (right parts of (6)—(8)).

As can be seen, the considered contributions are indeed negligible. This allows us to recommend parameters in Tables 1, 5—7 to be used in calculations of ΔH_f° of alkanepolythiols when at most one mercapto group is bound to the C atom. The barriers of internal rotation of methanethiol (5.3 kJ mol^{-1}),[38] ethanethiol (6.8 kJ mol^{-1}),[39] 2-propanethiol (5.8 kJ mol^{-1}),[40] and 2-methylpropanethiol-2 (5.7 kJ mol^{-1})[41] also confirm our conclusion because the barrier height depends slightly on the functional environment of the mercapto group.

Thus, the single force field for AlkSH, AlkSAlk′, and alkanepolythiols was proposed in the present work for the first time. The vibrational frequencies of many molecules were determined, and a good correspondence of the calculated and experimental values was obtained. Based on the calculated spectra, we assigned the vibrational frequencies of complicated molecules, whose spectra are insufficiently studied. The parameters for the calculations of $\Delta H_f^\circ(298)$, $S^\circ(298)$, and $C^\circ_p(T)$ were found in the framework of the additive-group approach. The presented coefficients for temperature dependence (a) allow the calculation of values of other thermodynamic functions for any molecule of these classes in the 298—1500 K temperature interval.

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Received April 2, 2001