Enthalpies of Combustion of 18 Organic Sulfur Compounds Related to Petroleum

WILLIAM D. GOOD

Bartlesville Energy Research Center, Bureau of Mines, U.S. Department of the Interior, Bartlesville, Okla. 74003

Enthalpies of combustion measured by rotating-bomb combustion calorimetry are given for 18 organic sulfur compounds including thiols, sulfides, thiophenes, and a disulfide selected for a comprehensive study of their thermodynamic properties. Values of the enthalpy of formation of the condensed phase are derived. Enthalpies of vaporization and enthalpies of formation in the gaseous state are derived for 15 of the compounds. Values of enthalpy of atomization are compared with values predicted by a correlation procedure.

In cooperation with the American Petroleum Institute, thermochemical studies of organic sulfur compounds, either occurring in or related to petroleum, were performed by the Bureau of Mines. The enthalpies of combustion of 18 of those compounds are summarized and interpreted in this paper. At the beginning of the program, no reliable method was available for the measurement of enthalpies of combustion of organic sulfur compounds, and a rotating-bomb combustion calorimeter (8) was built that provided a firm basis for organic sulfur compound combustion calorimetry. That calorimeter (8) and its successors (7) were used in this research.

EXPERIMENTAL

Apparatus and Procedures. The basic apparatus and procedures for combustion calorimetry of organic sulfur compounds have been described (8, 20), and only details pertinent to the present study are described here. The calorimeter and bomb used for each compound studied, the benzoic acid sample burned and the value of ϵ(cal) obtained, the value of $\Delta Ec^\circ/M$ for the auxiliary oil, and the description of the fuse used to initiate the reaction are summarized in Table I.

Three rotating-bomb calorimeters were used. The advantage of these calorimetric systems over conventional systems is provision for moving the bomb simultaneously about two axes

within the calorimetric vessel—both end over end and about its own axis. A relatively large volume of fluid may be placed within the bomb. Motion of the bomb hastens both the solution of inorganic combustion products and the establishment of equilibrium between the gaseous and aqueous phases. These modifications to the conventional bomb calorimeter have been made without significant loss of precision or accuracy. The precision of measurements, as measured by the standard deviation of the mean, is ordinarily 0.01% or better. The calorimeters designated BMR-I (8) and BMR-II (7) have been described. Calorimeter BMR-III is essentially identical with BMR-II. Two platinum-lined bombs, laboratory designations PT-4 (8) and Pt-3b (5), were alike except for their internal volumes. The changes of the effective internal volume of the bombs with change of electrodes and internal fittings are reflected in Table I.

Three different standard samples of benzoic acid used to calibrate the calorimetric system during these investigations are identified in Table I. The certified values of the heat of combustion of National Bureau of Standards Samples 39G, 39H, and 39I were 26433.8 ± 2.6, 26434 ± 3, and 26434 ± 3 abs J/g. Conversion to standard conditions (9) gives 6312.97 ± 0.62, 6313.02 ± 0.72, and 6313.02 ± 0.72 cal/g, respectively, for $-\Delta Ec^\circ/M$, the energy of the idealized combustion reaction.

One sample of hydrocarbon auxiliary oil, laboratory designation USBM-P3a and empirical formula $CH_{1.894}$, was used as a

Table I. Identification of Calorimetric System and Auxiliary Materials

	Calorimeter	Bomb (Vol, I)	Benzoic acid	ϵ(cal), cal/deg	$-\Delta Ec^\circ/M$ (oil), cal/g	Fuse
2-Methyl-1-butanethiol	BMR II	Pt 3b (0.3494)	39H	4008.54 ± 0.22 (9)[a]	10983.84 ± 0.20[b]	Thread
3-Methyl-1-butanethiol	BMR I	Pt 3b (0.3480)	39G	3898.93 ± 0.15 (8)	10983.70 ± 0.29	Paper
3-Methyl-2-butanethiol	BMR II	Pt 3b (0.3494)	39H	4005.77 ± 0.12 (10)	10983.83 ± 0.69	Thread
2,2-Dimethyl-1-propanethiol	BMR II	Pt 3b (0.3494)	39H	4008.54 ± 0.22 (9)	10983.84 ± 0.20	Thread
2,3-Dimethyl-2-butanethiol	BMR II	Pt 3b (0.3494)	39H	4008.72 ± 0.13 (9)	10983.83 ± 0.69	Thread
2-Methyl-2-pentanethiol	BMR II	Pt 3b (0.3494)	39H	4008.72 ± 0.13 (9)	10983.83 ± 0.69	Thread
Phenylmethanethiol	BMR II	Pt 3b (0.3494)	39H	4005.77 ± 0.12 (10)	10983.83 ± 0.69	Thread
Cyclohexanethiol	BMR I	Pt 3b (0.3480)	39G	3898.93 ± 0.15 (8)	10983.70 ± 0.29	Paper
2,2,5,5-Tetramethyl-3,4-dithiahexane	BMR II	Pt 3b (0.3494)	39I	4006.13 ± 0.29 (9)	10984.30 ± 0.15	Thread
2,4-Dimethyl-3-thiapentane	BMR II	Pt 3b (0.3502)	39H	4002.27 ± 0.09 (6)	10984.12 ± 0.51	Thread
2,2,4,4-Tetramethyl-3-thiapentane	BMR II	Pt 3b (0.3494)	39H	4008.72 ± 0.13 (9)	10983.83 ± 0.69	Thread
Cyclopentyl-1-thiaethane	BMR I	Pt 3b (0.3501)	39H	3898.55 ± 0.10 (10)	10984.18 ± 0.41	Thread
1-Phenyl-1-thiaethane	BMR II	Pt 3b (0.3494)	39H	4005.77 ± 0.12 (10)	10983.83 ± 0.69	Thread
2-Methylthiacyclopentane	BMR III	Pt 3b (0.3494)	39H	4025.68 ± 0.12 (8)	10984.12 ± 0.51	Thread
3-Methylthiacyclopentane	BMR II	Pt 3b (0.3494)	39H	4008.72 ± 0.13 (9)	10983.83 ± 0.69	Thread
2,3-Benzothiophene	BMR I	Pt 4 (0.3471)	39G	3908.80 ± 0.14 (8)	10983.70 ± 0.29	Paper
Dibenzothiophene	BMR III	Pt 3b (0.3494)	39H	4026.48 ± 0.31 (8)	$\ldots$[c]	Thread
2-Isopropylthiophene	BMR II	Pt 3b (0.3494)	39H	4008.54 ± 0.22 (9)	10983.84 ± 0.20	Thread

[a] Number of experiments. [b] Mean value with standard deviation. [c] No kindling material used.

kindling substance. The value of $\Delta Ec^\circ/M$ for the oil was determined several times, and the value used was obtained from a series of oil combustion experiments chronologically near the sulfur compound combustion experiments. The values of $\Delta Ec^\circ/M$ for the oil are listed in Table I. The amount of kindling material ordinarily is 20–50 mg, and inspection of the values of $\Delta Ec^\circ/M$ for the oil given in Table I reveals that little or no error would have resulted if the same value of $\Delta Ec^\circ/M$ had been used throughout.

Two materials served as fuses to initiate the combustion reaction. The value of $\Delta Ec^\circ/M$ for the material used earlier, filter paper of empirical formula $CH_{1.686}O_{0.842}$, was -3923 cal/g. $\Delta Ec^\circ/M$ for the material used later, cotton thread of empirical formula $CH_{1.774}O_{0.887}$, was -4050 cal per gram. About 10 ml of distilled water was added to the bomb for each combustion series. One atmosphere of air was left in the bomb which was subsequently charged with pure oxygen to a total pressure of 30 atm.

Nitric acid, nitrous acid, and total acids were determined quantitatively in the combustion products (8, 20). The amount of sulfuric acid was obtained by difference. No evidence for thermally significant SO_2 or for sulfuric acid attack on the borosilicate glass ampuls or bomb was found (20).

Fragile ampuls of borosilicate glass confined all the liquid compounds and one solid compound, 2,3-benzothiophene. However, dibenzothiophene, solid at room temperature, was burned in the form of pellets. Each experiment was begun at 23°C, and because of the masses of combustibles chosen, the final temperatures were nearly 25°C.

Materials. All samples except 2-isopropylthiophene were from materials purified for the API Standard Sample Repository (American Petroleum Institute Research Project 58 at Carnegie-Mellon University) by the Bureau of Mines Laramie Energy Research Center, Laramie, Wyo.

Table II gives values of purity for the 18 samples. Purities of several of the compounds were estimated from freezing temperature vs. fraction melted curves observed by the Low-Temperature Calorimetry Group at the Bartlesville Energy Research Center. Purities of several other compounds were estimated by means of gas-liquid chromatography and spectroscopy at the Bureau of Mines Laramie Energy Research Center. Careful gas-liquid chromatographic analysis identified 0.35% of light hydrocarbon impurities in the sample of 2-isopropylthiophene.

Sulfuric acid was recovered from the combustion products of all compounds. The recoveries are given in Table II. Quantitative recovery of sulfuric acid has proved to be difficult (8), but the $99+\%$ recoveries do tend to confirm the purities of the sulfur compounds. Uncertainty in the sulfuric acid recovery probably is higher than the 0.1–0.3% average deviations given in Table II. All compounds except 2,3-benzothiophene and dibenzothiophene were dried by passing the vapor over activated molecular sieve. 2,3-Benzothiophene was dried by liquid contact with CaH_2. The crystalline dibenzothiophene was studied without further drying.

For reducing weights in air to masses and converting the energy of the actual bomb process to that of the isothermal process and reducing to standard states (9), the values summarized in Table II were used for density, ρ, the change of internal energy with pressure, $(\partial E/\partial P)_T$, and heat capacity, c_p. Research of API Research Project 48 at the Bureau of Mines Laramie Energy Research Center gave values of density for most of the compounds. Values of $(\partial E/\partial P)_T$ were calculated from the temperature dependence of density by using the approximation $(\partial E/\partial P)_T = -T(\partial V/\partial T)_P$. For a few compounds whose density had not been measured, values were obtained either from the mass of pellet of known volume or from the mass of a known volume of liquid (the ampuls for combustion). Values of c_p for several compounds were measured by the Low-Temperature Calorimetry Group at the Bartlesville Energy Research Center. The other values of c_p were estimated from values for structurally similar compounds.

Units of Measurements. The experimental results reported are based on the 1961 atomic weights (1) and the 1963 definition of the thermochemical calorie (cal = 4.184 J) (2). The reference temperature is 25°C.

Calorimetric Results. Typical combustion experiments for each of the 18 compounds are summarized in Table III. It is impractical to list summaries for all experiments, but values of $\Delta Ec^\circ/M$ for all experiments are given in Table IV. All values of $\Delta Ec^\circ/M$ in Tables III and IV refer to the generalized combustion reaction

$$C_aH_bS_c(l \text{ or } c) + (a + b/4 + 3\,c/2)O_2(g) +$$
$$(nc + c - b/2)H_2O(l) = aCO_2(g) + c(H_2SO_4 \cdot nH_2O)(l) \quad (1)$$
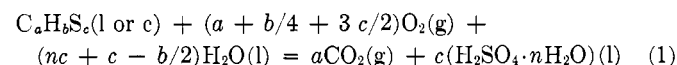
Values of n and of the initial number of moles of water placed in the bomb are listed in Table III. The values for 2,3-benzothiophene and dibenzothiophene are for the crystalline state. All other values are for the liquid state.

Table II. Compound Description

Compound	Formula	Purity, mol %	H_2SO_4 recovery, % of theoretical	ρ, g/ml	$(\partial E/\partial P)_T$, cal/atm/g	c_p, cal/g/deg
2-Methyl-1-butanethiol	$C_5H_{12}S$	99.9 ± 0.1[a]	100.0 ± 0.1	0.84196[b]	−0.0066	(0.46)
3-Methyl-1-butanethiol	$C_5H_{12}S$	99.95[c]	100.0 ± 0.1	0.83161[b]	−0.0066	0.460
3-Methyl-2-butanethiol	$C_5H_{12}S$	99.996[c]	99.5 ± 0.3	0.83606[b]	−0.0067	0.456
2,2-Dimethyl-1-propanethiol	$C_5H_{12}S$	99.9 ± 0.1[a]	100.0 ± 0.2	0.82546[b]	−0.0068	(0.46)
2,3-Dimethyl-2-butanethiol	$C_6H_{14}S$	99.9 ± 0.1[a]	99.2 ± 0.2	0.83997[b]	−0.0063	(0.46)
2-Methyl-2-pentanethiol	$C_6H_{14}S$	99.9 ± 0.1[a]	99.2 ± 0.2	0.82209[b]	−0.0064	(0.46)
Phenylmethanethiol	C_7H_8S	99.97 ± 0.03[a]	99.3 ± 0.1	1.05143[b]	−0.0062	(0.39)
Cyclohexanethiol	$C_6H_{12}S$	99.978[c]	99.8 ± 0.1	0.94402[b]	−0.0063	0.396
2,2,5,5-Tetramethyl-3,4-dithiahexane	$C_8H_{18}S_2$	99.98 ± 0.02[a]	100.0 ± 0.1	0.919[d]	(−0.0069)[e]	(0.42)
2,4-Dimethyl-3-thiapentane	$C_6H_{14}S$	99.992[c]	100.0 ± 0.1	0.81031[b]	−0.0066	0.470
2,2,4,4-Tetramethyl-3-thiapentane	$C_8H_{18}S$	99.94 ± 0.03[a]	99.3 ± 0.2	0.82207[b]	−0.0059	(0.46)
Cyclopentyl-1-thiaethane	$C_6H_{12}S$	99.986[c]	99.6 ± 0.2	0.93769[b]	−0.0064	0.397
1-Phenyl-1-thiaethane	C_7H_8S	99.97[c]	99.5 ± 0.1	1.05392[b]	−0.0065	(0.39)
2-Methylthiacyclopentane	$C_5H_{10}S$	99.76[c]	99.5 ± 0.1	0.95046[b]	−0.0068	0.402
3-Methylthiacyclopentane	$C_5H_{10}S$	99.95[c]	99.4 ± 0.1	0.95823[b]	−0.0065	0.404
2,3-Benzothiophene	C_8H_6S	99.968 ± 0.010[a]	99.9 ± 0.2	1.165[d]	(−0.005)	(0.29)
Dibenzothiophene	$C_{12}H_8S$	99.95 ± 0.03[a]	99.6 ± 0.2	1.182[d]	(−0.003)	(0.29)
2-Isopropylthiophene	$C_7H_{10}S$	99.65[f]	99.6 ± 0.1	0.963[d]	−0.0070	(0.40)

[a] Purity estimated by API Research Project 48, Laramie Energy Research Center, by means of gas-liquid chromatography and spectroscopy. [b] Unpublished measurements of API Project 48, Laramie Energy Research Center. [c] Purity estimated from freezing temperature vs. fraction melted curves by Low-Temperature Calorimetry Group at Bartlesville Energy Research Center. [d] Value obtained by weighing ampul or pellet of known volume. [e] Values in parentheses are estimates. [f] Purity estimated by gas-liquid chromatography.

Derived molal values of $\Delta Ec°$, the energy of the idealized combustion reaction, $\Delta Hc°$, the standard enthalpy of combustion, and $\Delta Hf°$, the standard enthalpy of formation, are given in Table V. The values of $\Delta Ec°$ and $\Delta Hc°$ refer to Reaction 1 at 298.15°K. The values of $\Delta Hf°$ refer to Reaction 2 at 298.15°K.

$$aC(c, \text{graphite}) + b/2H_2(g) + cS(rh) = C_aH_bS_c(l, c, \text{or } g) \quad (2)$$
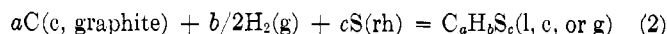
Uncertainties given are the "uncertainty interval" (18) defined as twice the final overall standard deviation of the mean. The "uncertainty interval" reflects uncertainty in the calibration experiments, in the compound combustion experiments, and in the enthalpies of formation of the combustion products. The enthalpies of formation of gaseous CO_2 and liquid H_2O were taken to be -94.051 and -68.315 kcal/mol, respectively (21).

The values of the enthalpy of formation of $H_2SO_4 \cdot nH_2O$ were interpolated from the table of reference (21). Uncertainties assigned to gaseous CO_2 (19), liquid H_2O (17), and $H_2SO_4 \cdot nH_2O$ (6, 14) were 0.011, 0.010, and 0.046 kcal/mol, respectively.

Vapor pressure measurements were reported for 12 of the compounds (16), and the vapor pressures of phenylmethanethiol and 2,2,4,4-tetramethyl-3-thiapentane have been measured. Values of the enthalpy of vaporization at 298.15°K were computed from the Cox equations (3), the exact form of the Clapeyron equation and estimated values of the second virial coefficient. These values of the enthalpy of vaporization, Table V, are strictly the enthalpy of vaporization to the real gas, $\Delta Hv_{298.15}$, but are not significantly different from the standard enthalpy of vaporization, $\Delta Hv°_{298.15}$. The value of the enthalpy of vaporization of 2,2,5,5-tetramethyl-3,4-dithiahexane is an estimate (13).

Table III. Summary of Typical Calorimetric Experiments at 298.15°K[a]

Thiols

	2-Methyl-1-butane-thiol	3-Methyl-1-butane-thiol	3-Methyl-2-butane-thiol	2,2-Dimethyl-1-propane-thiol	2,3-Dimethyl-2-butane-thiol	2-Methyl-2-pentane-thiol	Phenyl-methane-thiol	Cyclo-hexane-thiol	Disulfide 2,2,5,5-Tetra-methyl-3,4-dithiahexane
m' (compound), gram	0.830005	0.75950	0.828467	0.820261	0.726980	0.749190	0.892562	0.80936	0.837252
m'' (oil), gram	0.019471	0.05553	0.018503	0.029500	0.093683	0.073584	0.022449	0.02403	0.048787
m''' (fuse), gram	0.001188	0.00417	0.001025	0.001121	0.000986	0.001285	0.001004	0.00395	0.001159
$\Delta t_c = t_f - t_i + \Delta t_{cor}$, deg	2.00688	1.99756	1.99956	2.00613	2.00113	1.99930	1.99966	2.00049	1.99467
$n_i(H_2O)$, mole	0.5526	0.5535	0.5529	0.5526	0.5524	0.5524	0.5529	0.5535	0.5526
$H_2SO_4 \cdot n \ H_2O$ (Eq 1)	$n = 75$	$n = 80$	$n = 70$	$n = 75$	$n = 100$	$n = 90$	$n = 80$	$n = 90$	$n = 60$
$\varepsilon(\text{cal})(-\Delta t_c)$, cal	-8044.66	-7788.35	-8009.78	-8041.65	-8021.97	-8014.63	-8010.18	-7799.77	-7990.91
$\varepsilon(\text{cont})(-\Delta t_c)$, cal[b]	-27.66	-27.64	-28.25	-27.65	-27.73	-28.17	-28.16	-27.73	-28.07
ΔE_{ign}, cal	0.63	1.35	0.40	0.43	0.43	0.41	0.40	1.35	0.53
ΔE_{dec} (HNO$_3$), cal	10.36	11.16	10.88	10.16	11.28	12.42	6.50	9.83	12.40
$\Delta E_{f,diln}$ (H$_2$SO$_4$), cal	-0.01	0.03	0.12	0.01	-0.05	0.08	0.00	-0.10	0.12
$\Delta E_{cor\ to\ std\ states}$, cal[c]	2.49	2.59	2.50	2.55	3.22	3.12	5.10	3.34	2.35
$-m'' \ \Delta Ec°/M$ (oil), cal	213.86	609.92	203.23	324.02	1029.00	808.23	246.57	263.94	535.89
$-m''' \Delta Ec°/M$ (fuse), cal	4.81	16.36	4.15	4.54	3.99	5.20	4.07	15.50	4.69
$m' \ \Delta Ec°/M$ (compd), cal	-7840.18	-7174.58	-7816.75	-7727.59	-7001.83	-7213.34	-7775.70	-7533.64	-7463.00
$\Delta Ec°/M$ (compd), cal g^{-1}	-9445.94	-9446.44	-9435.20	-9420.89	-9631.39	-9628.18	-8711.66	-9308.15	-8913.67

Sulfides

	2,4-Dimethyl-3-thia-pentane	2,2,4,4-Tetra-methyl-3-thia-pentane	Cyclo-pentyl-1-thia-ethane	1-Phenyl-1-thia-ethane	2-Methyl-thiacyclo-pentane	3-Methyl-thiacyclo-pentane	Thiophenes 2,3-Benzo-thiophene[d]	Dibenzo-thiophene[d]	2-Iso-propyl-thiophene
m' (compound), gram	0.80112	0.719537	0.75794	0.889184	0.77770	0.840574	0.75203	0.96878	0.833739
m'' (oil), gram	0.03532	0.081487	0.06430	0.023979	0.08960	0.078432	0.14423	. . .	0.046324
m''' (fuse), gram	0.00122	0.001298	0.00115	0.001040	0.00103	0.001084	0.00376	0.00098	0.001191
$\Delta t_c = t_f - t_i + \Delta t_{cor}$, deg	2.02473	2.00288	2.00087	1.99942	1.99605	2.11792	2.01751	2.05137	2.00860
$n_i(H_2O)$, mole	0.5535	0.5524	0.5535	0.5529	0.5535	0.5524	0.5534	0.5535	0.5526
$H_2SO_4 \cdot n \ H_2O$ (Eq 1)	$n = 90$	$n = 120$	$n = 90$	$n = 80$	$n = 80$	$n = 70$	$n = 95$	$n = 110$	$n = 85$
$\varepsilon(\text{calor})(-\Delta t_c)$, cal	-8103.52	-8028.98	-7800.49	-8009.22	-8035.46	-8490.15	-7886.04	-8259.80	-8051.55
$\varepsilon(\text{cont})(-\Delta t_c)$, cal[b]	-28.68	-27.74	-27.47	-28.20	-27.69	-29.35	-27.61	-28.14	-27.63
$\Delta E_{f,ign}$, cal	0.33	0.49	1.07	0.40	0.82	0.47	1.35	0.69	0.51
$\Delta E_{f,dec}$ (HNO$_3$), cal	12.56	10.11	8.75	6.57	7.61	9.79	9.72	8.61	8.28
$\Delta E_{f,diln}$ (H$_2$SO$_4$), cal	0.00	0.02	0.02	0.01	0.00	0.04	0.12	-0.02	0.05
$\Delta E_{cor\ to\ std\ states}$, cal[c]	2.92	3.70	3.46	5.09	3.33	3.38	6.10	7.63	4.56
$-m'' \ \Delta Ec°/M$ (oil), cal	387.96	995.04	706.28	263.38	984.18	861.48	1584.18	. . .	508.81
$-m''' \ \Delta Ec°/M$ (fuse), cal	4.94	5.26	4.66	4.21	4.17	4.39	14.75	3.97	4.82
$-m'''' \ \Delta Ec°/M$ (impurities)									31.85
$m' \ \Delta Ec°/M$ (compd), cal	-7723.49	-7142.10	-7103.72	-7757.76	-7063.04	-7639.95	-6297.43	-8267.06	-7520.30
$\Delta Ec°/M$ (compd), cal g^{-1}	-9640.87	-9925.97	-9372.40	-8724.58	-9081.96	-9088.97	-8373.91	-8533.47	-9019.97

[a] The symbols and abbreviations of this table are those of reference 9 except as noted. [b] $\varepsilon_i(\text{cont})(t_i - 25°C) + \varepsilon_f(\text{cont})(25° - t_f + \Delta t_{cor})$. [c] Items 81–85, 87–90, 93, and 94 of the computation form of reference 9. [d] Values for the crystalline state.

Values of the enthalpy of vaporization were combined with values of the enthalpy of formation in the condensed state, Table V, to derive the enthalpy of formation in the ideal gaseous state.

DISCUSSION

Comparison with Previous Work. Five of the compounds were studied earlier by H. Mackle and co-workers (10–13). A comparison of the earlier values of enthalpies of formation in the liquid state with those of this research is given in Table VI. Agreement of values for three compounds is within the combined experimental uncertainty, and values for two compounds differ by slightly more than their combined uncertainties. No explanation for the disagreement can be offered.

Correlation of Enthalpies of Atomization. Cox and Pilcher (4) recently correlated the existing enthalpies of atomization of the organic sulfur compounds. The parameters given by Cox and Pilcher (4) were used along with the value of

Table IV. Summary of Experimental Results. Values of $\Delta Ec°/M$ at 298.15°K

	Thiols								Disulfide
	2-Methyl 1-butane-thiol	3-Methyl-1-butane-thiol	3-Methyl-2-butane-thiol	2,2-Dimethyl-1-propane-thiol	2,3-Dimethyl 2-butane-thiol	2-Methyl-2-pentane-thiol	Phenyl-methane-thiol	Cyclo-hexane-thiol	2,2,5,5-Tetra-methyl-3,4-dithiahexane
	−9447.28	−9445.66	−9436.74	−9422.66	−9631.70	−9626.90	−8713.16	−9307.38	−8913.67
	−9444.03	−9444.78	−9437.16	−9420.89	−9631.39	−9628.03	−8711.01	−9308.26	−8911.93
	−9444.45	−9446.87	−9436.11	−9420.46	−9631.20	−9628.18	−8713.35	−9308.95	−8913.18
	−9443.57	−9442.13	−9435.20	−9418.77	−9630.05	−9628.29	−8708.29	−9307.13	−8913.93
	−9446.13	−9452.03	−9432.70	−9419.73	−9630.93	−9630.72	−8710.54	−9306.08	−8912.24
	−9448.19	−9444.88		−9420.75	−9630.05	−9625.34	−8713.98	−9308.15	−8911.89
	−9445.94	−9446.44		−9420.60	−9630.55	−9628.08	−8711.66	−9306.78	−8913.20
	−9447.45			−9421.27		−9628.22			−8911.63
									−8914.40
Mean	−9445.88	−9446.11	−9435.58	−9420.64	−9630.84	−9627.97	−8711.71	−9307.53	−8912.90
Std dev	±0.61	±1.14	±0.79	±0.40	±0.24	±0.53	±0.75	±0.37	±0.34

	Sulfides						Thiophenes		
	2,4-Dimethyl-3-thia-pentane	2,2,4,4-Tetra-methyl-3-thiopentane	Cyclo-pentyl-1-ethane	1-Phenyl-1-thia-ethane	2-Methyl-thiacyclo-pentane	3-Methyl-thiacyclo-pentane	2,3-Benzo-thiophene[a]	Dibenzo-thiophene[a]	2-Isopropyl-thiophene
	−9640.87	−9925.97	−9371.90	−8724.63	−9083.11	−9088.97	−8373.91	−8532.65	−9019.27
	−9645.14	−9926.51	−9372.40	−8723.89	−9079.18	−9087.62	−8372.40	−8533.47	−9019.97
	−9640.28	−9924.26	−9370.71	−8725.53	−9082.23	−9088.03	−8372.60	−8532.68	−9018.81
	−9640.78	−9926.32	−9371.00	−8724.91	−9080.80	−9086.26	−8372.48	−8533.22	−9020.43
	−9644.47	−9925.21	−9367.78	−8725.23	−9081.77	−9087.53	−8370.58	−8534.96	−9020.37
	−9640.81	−9924.25	−9372.72	−8724.09	−9081.96	−9087.55	−8372.35	−8535.15	−9021.95
	−9641.49	−9926.12		−8724.58	−9080.46	−9086.56	−8369.95	−8533.43	−9020.05
	−9640.88					−9087.61	−8370.39	−8532.88	−9022.75
								−8533.15	
								−8534.64	
Mean	−9641.84	−9925.52	−9371.09	−8724.69	−9081.36	−9087.52	−8371.83	−8533.62	−9020.45
Std dev	±0.66	±0.36	±0.73	±0.22	±0.49	±0.30	±0.48	±0.28	±0.46

[a] Values for the crystalline state.

Table V. Molal Values at 298.15°K, Kcal/Mol

Compound	n	$\Delta Ec°$ (l or c)[a]	$\Delta Hc°$ (l or c)[a]	$\Delta Hf°$ (l or c)[a]	$\Delta Hv°$	$\Delta Hf°$ (g)
2-Methyl-1-butanethiol	75	−984.41 ± 0.20	−987.07 ± 0.20	−36.83 ± 0.22	9.41 ± 0.05	−27.42 ± 0.23
3-Methyl-1-butanethiol	80	−984.43 ± 0.26	−987.10 ± 0.26	−36.82 ± 0.28	9.42 ± 0.05	−27.40 ± 0.28
3-Methyl-2-butanethiol	70	−983.33 ± 0.20	−986.00 ± 0.20	−37.87 ± 0.22	8.96 ± 0.05	−28.91 ± 0.23
2,2-Dimethyl-1-propanethiol	75	−981.78 ± 0.18	−984.44 ± 0.18	−39.46 ± 0.20	8.70 ± 0.05	−30.76 ± 0.21
2,3-Dimethyl-2-butanethiol	100	−1138.77 ± 0.16	−1141.74 ± 0.16	−44.61 ± 0.19	9.39 ± 0.05	−35.22 ± 0.20
2-Methyl-2-pentanethiol	90	−1138.44 ± 0.20	−1141.40 ± 0.20	−44.92 ± 0.23	9.55 ± 0.05	−35.37 ± 0.24
Phenylmethanethiol	80	−1082.05 ± 0.24	−1084.12 ± 0.24	+8.73 ± 0.26	13.53 ± 0.05	22.26 ± 0.27
Cyclohexanethiol	90	−1081.78 ± 0.16	−1084.45 ± 0.16	−33.55 ± 0.19	10.67 ± 0.05	−22.88 ± 0.19
2,2,5,5-Tetramethyl-3,4-dithia-hexane	60	−1589.71 ± 0.32	−1594.16 ± 0.32	−60.46 ± 0.36	12.71 ± 0.40[b]	−47.75 ± 0.54
2,4-Dimethyl-3-thiapentane	90	−1140.08 ± 0.20	−1143.04 ± 0.20	−43.28 ± 0.23	9.47 ± 0.05	−33.81 ± 0.24
2,2,4,4-Tetramethyl-3-thiapentane	120	−1452.07 ± 0.22	−1455.63 ± 0.22	−55.51 ± 0.26	10.46 ± 0.05	−45.05 ± 0.27
Cyclopentyl-1-thiaethane	90	−1089.17 ± 0.20	−1091.84 ± 0.20	−26.16 ± 0.22	10.78 ± 0.05	−15.38 ± 0.23
1-Phenyl-1-thiaethane	80	−1083.66 ± 0.14	−1085.73 ± 0.14	+10.35 ± 0.17	12.98 ± 0.05	23.33 ± 0.18
2-Methylthiacyclopentane	80	−928.11 ± 0.15	−930.48 ± 0.15	−25.13 ± 0.17	9.86 ± 0.05	−15.27 ± 0.18
3-Methylthiacyclopentane	70	−928.72 ± 0.14	−931.11 ± 0.14	−24.45 ± 0.17	10.07 ± 0.05	−14.38 ± 0.18
2,3-Benzothiophene	95	−1123.51 ± 0.19	−1125.29 ± 0.19	+24.11 ± 0.22	...	...
Dibenzothiophene	110	−1572.42 ± 0.32	−1574.49 ± 0.32	+28.76 ± 0.35	...	...
2-Isopropylthiophene	85	−1138.58 ± 0.43[c]	−1140.95 ± 0.43[c]	−2.77 ± 0.44	...	...

[a] All values are for the liquid state except 2,3-benzothiophene and dibenzothiophene. [b] Reference 13. [c] Uncertainty interval doubled because of impurity.

Table VI. Comparison of Values of $\Delta Hf°_{298.15}$ (Liquid) with Earlier Literature Values, Kcal/Mol

Compound	$\Delta Hf°_{298.15}$, this research	$\Delta Hf°_{298.15}$, lit
Phenylmethanethiol	$+8.73 \pm 0.26$	10.57 ± 0.50 (12)
2,2,5,5-Tetramethyl-3,4-dithiahexane	-60.46 ± 0.36	-59.84 ± 0.42 (13)
2,4-Dimethyl-3-thiapentane	-43.28 ± 0.23	-43.49 ± 0.51 (11)
2,2,4,4-Tetramethyl-3-thiapentane	-55.51 ± 0.26	-55.54 ± 0.20 (11)
1-Phenyl-1-thiaethane	$+10.35 \pm 0.17$	$+11.50 \pm 0.50$ (10)

Table VII. Estimated and Observed Enthalpies of Atomization of Organic Sulfur Compound at 298.15°K, Kcal

	ΔHa(obs)	ΔHa(est)	ΔHa (est) − ΔHa(obs)
2-Methyl-1-butanethiol	1572.77	1572.77	0.00
3-Methyl-1-butanethiol	1572.75	1572.77	0.02
3-Methyl-2-butanethiol	1574.26	1574.87	0.61
2,2-Dimethyl-1-propanethiol	1576.11	1576.88	0.77
2,3-Dimethyl-2-butanethiol	1855.67	1857.22	1.55
2-Methyl-2-pentanethiol	1855.82	1855.79	−0.03
Cyclohexanethiol	1739.13	1738.86	−0.27
2,2,5,5-Tetramethyl-3,4-dithiahexane	2484.05	2482.97	−1.08
2,4-Dimethyl-3-thiapentane	1854.26	1854.57	0.31
2,2,4,4-Tetramethyl-3-thiapentane	2415.70	2420.47	4.77
Cyclopentyl-1-thiaethane	1731.63	1730.95	−0.68
2-Methylthiacyclopentane	1856.42	1856.26	−0.16
3-Methylthiacyclopentane	1455.53	1456.19	0.66

the ring strain energy for thiacyclopentane (15) to calculate enthalpies of atomization for the saturated compounds studied in this research. Calculated values and experimental values are compared in Table VII. Except for 2,2,4,4-tetramethyl-3-thiapentane with its high steric interaction energy, the fit of the correlation is good.

ACKNOWLEDGMENT

NOMENCLATURE

∂ = differential operator
m = mass, grams
n = number of moles
P = pressure, atm
T = temperature, °K
t = temperature, °C
ε (cal) = heat equivalent of calorimeter, cal/°K
ε (cont) = heat equivalent of contents, cal/°K
ΔE_{dec} = energy of decomposition, cal
ΔE_{ign} = electrical ignition, energy, cal
$\Delta E_{cor\ to\ std\ states}$ = energy for reduction to standard states, cal

$\Delta Ec°/M$ = standard energy of idealized combustion reaction, cal/g
$\Delta Ec°$ = standard energy of idealized combustion reaction, kcal/mol
$\Delta Hc°$ = standard enthalpy of combustion, kcal/mol
$\Delta Hf°$ = standard enthalpy of formation, kcal/mol
$\Delta Hv°$ = standard enthalpy of vaporization, kcal/mol
ΔHa = enthalpy of atomization, kcal/mol
Δt_c = corrected temperature rise, °C

SUBSCRIPTS

i = initial state
f = final state

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