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Heats of Combustion and Formation of the *n*-Alkane-α,ω-dithiols from Ethane through Pentane

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The heats of combustion of four *n*-alkane-α,ω-dithiols have been determined and therefrom values of the standard heats of formation, $\Delta H°$(liq), at 25°C, have been derived. From heat of vaporization measurements standard heat of formation values for the gaseous compounds, $\Delta H°_f$ (g), have been calculated. The obtained data are, for the liquid and gaseous states,

ethanedithiol-1,2: −12.91 and − 2.23;
propanedithiol-1,3: −18.90 and − 7.03;
butanedithiol-1,4: −25.20 and − 12.03;
pentanedithiol-1,5: −31.04 and − 16.87
kcal.mole^{-1}, respectively.

It is possible that in the near future agreement may be reached on the use of a slightly different value for the heat of formation of sulphuric acid, $\Delta H°_f$ (H_2SO_4, 115 H_2O) = a. In this case, the published values should be corrected by adding the quantity $2(a + 212.24)$ kcal. mole^{-1}.

In the experimental determination of the strain energy [1] of the dithiolane ring structure, by comparing the heat of oxidation of propanedithiol-1,3 with that of an alkane thiol to form dithiolane and an open dialkyl disulfide, respectively, it was assumed that the two thiol groups in the propanedithiol-1,3 behave energetically like thiol groups in separate molecules, *i.e.* intramolecular interactions between the thiol groups should be absent. In order to verify this, in itself very reasonable, assumption determinations of heats of combustion of a number of alkane-α,ω-dithiols were undertaken.

EXPERIMENTAL

Synthesis and purification of compounds

The dithiols were all synthesized by conversion of the corresponding dibromides to the bis-isothiouronium hydrobromides and subsequent hydrolysis using KOH [2,3].

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The compounds were purified by repeated vacuum-distillation in a 50 cm column packed with glass helices at several pressures and in a nitrogen atmosphere. The purities of the fractions obtained were estimated by titration with iodine. Samples were sealed under nitrogen into small glass vials, which were broken under ethanol and titrated with 0.1 N iodine. The average deviation in a set of 4 titrations was found to correspond to an error in the purity of ± 0.1 %. From the results it is seen that only the titration on butanedithiol-1,4 indicated 100 % purity. Efforts to increase the purity of the other three dithiols as judged from iodine titrations were fruitless and it was concluded that the oxidation reaction in these cases was not quantitative. The same trend was observed by Grogan, Rice and Reid [4].

Ethanedithiol [2]. Distilled at 36 and 17 mm Hg, b.p. 61 and 45.8°C, respectively. Iodine titration 99.5 %.

Propanedithiol [3]. Distilled at 11 and 18 mm Hg, b.p. 51.8 and 67.0°C, respectively. Iodine titration 99.5 %.

Butanedithiol [3]. Distilled four times, the last two at 5 and 10 mm Hg, b.p. 61.6 and 71.7°C, respectively. Iodine titration 100. 1 %.

Pentanedithiol [3]. Distilled at 10 and 5.5 mm Hg, b.p. 89.0—89.2 and 81.7°C, respectively. Iodine titration 99.6 %.

The purities of the samples used for combustion studies were estimated from melting curves. These were determined using a simple "constant" heat input, thin layer method [8] using a calibrated platinum resistance thermometer *. The values obtained for the melting interval tend to be too high, particularly for low melting substances. Measurements on samples with known amounts of impurity added showed an increase in the melting interval of about 0.2°C per 0.1 mole % of impurity.

Table 1 gives estimated melting points for zero impurity and the purity of the samples as judged from the melting curves together with the results of density and refractive index measurements at 20 and 25°C.

Table 1.

Compound and reference	Density		Refractive index		M.p. °C	Estimated purity mole-%
	d_4^{20}	d_4^{25}	n_D^{20}	n_D^{25}		
Ethanedithiol-1,2.						
S. Mathias [5]	1.1243	1.1185	1.5590	—	—	
W.P. Hall and E.E. Reid [3]	—	1.1192	—	1.5558	—41.2	
S. Mathias [6]	—	1.11926	—	1.55632	—	
This work	1.1240_5	1.1189_4	1.5588_2	1.5562_8	—49.10	>99.8
Propanedithiol-1,3.						
S. Mathias [5]	1.0783	—	1.5406	—	—	
W.P. Hall and E.E. Reid [3]	—	1.0775	—	1.5371	—79	
Yu.K.Yur'ev and I.S.Levi [7]	1.0772	—	1.5392	—	—	
S. Mathias [6]	—	1.07338	—	1.53798	—	
This work	1.0779_6	1.0731_3	1.5406_2	1.5384_0	—90.65	>99.8
Butanedithiol-1,4.						
W.P. Hall and E.E. Reid [3]	—	1.0395	—	1.5265	—53.9	
S. Mathias [6]	—	1.03870	—	1.52724	—	
This work	1.0429_9	1.0385_2	1.5294_0	1.5273_8	—52.55	>99.8
Pentanedithiol-1,5.						
W.P. Hall and E.E. Reid [3]	—	1.0158	—	1.5194	—72.5	
S. Mathias [6]	—	1.01117	—	1.51799	—	
This work	1.0159_6	1.0115_8	1.5204_3	1.5183_9	—68.50	>99.9

* The 20 × 4 mm thermometer sealed in glass was not free from strain and showed a hysteresis effect. The absolute values of the given melting points therefore cannot be relied upon to better than ± 0.1°C.

Combustion calorimetry

Apparatus and procedure. The calorimetric system used was that described by Bjellerup [9]. The volatile liquid combustion samples were sealed in thin soft-glass ampoules. A platinum baffle was placed on top of the crucible to prevent splashing upon ignition. In combustion experiments with the dithiols the bomb was charged with 10 ml of water (in calibration experiments and paraffin oil combustions 0.79 ml). The amount of sulphur was limited to 5—7 m.atoms per experiment. All weighings have been reduced to mass and the molecular weights have been computed from the 1957 table of atomic weights [10].

The bomb liquid was analyzed for nitric and nitrous acids. The (HNO_3 + HNO_2)-content was determined by reduction with Devardas alloy [11]. Nitrous acid was measured colorimetrically according to a method by Griess [12(p. 38)]. The amount of nitric acid formed in benzoic acid and paraffin oil combustions was determined by potentiometric titration against 0.02 N NaOH.

Materials. The benzoic acid used in the calibration experiments was National Bureau of Standards standard sample 39h [13].

The paraffin oil used as auxiliary material was sample USBM-P3a, described in Ref.[9(p. 1531)].

The dithiol samples were dried over calcium sulphate and thereafter distilled at room temperature under reduced pressure into a receiver containing twelve glass ampoules. Dry nitrogen was introduced slowly, thereby forcing the liquid samples into the ampoules, and great care was taken to exclude air and moisture. The ampoules were sealed immediately, and in no case did more than four days pass between ampoule filling and combustion experiment.

Combustions in which the substance did not burn properly have all been rejected. The butanedithiol was particularly difficult to burn appropriately, which is apparent from the final over-all standard deviation figure.

RESULTS

Unit of energy. Auxiliary quantities. The results are expressed in terms of the defined thermochemical calorie equal to 4.1840 abs. joules. All symbols used are those introduced by Hubbard, Scott and Waddington [14]. The $(\partial E/\partial P)_T$ values were calculated from the corresponding density data using the approximate relation $(\partial E/\partial P)_T = -T(\partial V/\partial T)_P$. The $-\Delta E_c^\circ/M$ values refer to the reaction represented by eqn. 1, in which all reactants and products are in their thermodynamic standard states at the temperature t_h (25.0°C):

$$C_nH_{2n+2}S_2(\text{liq}) + (3n+7)/2\ O_2(\text{g}) + (231-n)\ H_2O(\text{liq}) \rightarrow \rightarrow n\ CO_2(\text{g}) + 2\ H_2SO_4,\ 115\ H_2O\ (\text{liq}) \quad (1)$$

In calibration experiments the certified value for the heat of combustion for the benzoic acid under certificate conditions $-\Delta E_c/M = 6317.88 \pm 0.72$ cal.g^{-1} was used. The standard heats of combustion were, for paraffin oil USBM-P3a $-\Delta E_c^\circ/M(\text{Oil}) = 10984.7 \pm 1.1$ cal.g^{-1}, and for the fuse $-\Delta E_c^\circ/M(\text{Fuse}) = 3971 \pm 4$ cal.g^{-1}.

Calculation of results. The results of the combustion experiments were calculated by use of the following main equations,

$$\varepsilon(\text{Calor}) = \varepsilon^\circ(\text{Calor}) - c_p(H_2O) \cdot m^i(\text{Cont.}) \quad (2)$$

$$-\Delta E_{\text{I.B.P}} = [\varepsilon(\text{Calor}) + \varepsilon^i(\text{Cont.})] \cdot \Delta t \quad (3)$$

$$-\Delta E_c^\circ/M(\text{Comp}) = \frac{1}{m'} \{-\Delta E_{\text{I.B.P.}} - [\Delta E^f_{\text{decomp.}}\ (HNO_3 + HNO_2) -$$

Table 2. Heat of combustion measurements.

t_h = 25.0°C V(Bomb) = 0.2628 liter m(Pt) = 18.579—18.587 g.
t_i = 24.1°C V^i(soln) = 0.01002 liter m(glass) = 0.055—0.085 g.
P^i(gas) = 30.0 atm. V^i(gas) = 0.2522 liter $m''' = 0.0045$—0.0056 g.

Compound	m' g	m'' g	Δt deg	$\Delta E^f_{dec.}(HNO_3 + HNO_2)$ cal	ΔE_{corr} cal	$-E^\circ_c/M$ cal.g^{-1}
Ethanedithiol-1,2	0.322188	0.248054	0.88098	5.80	1.32	7060.97
M = 94.202	0.319014	0.248649	0.87807	7.26	1.38	7061.10
m^i(Cont.) = 39.28 g	0.337311	0.237454	0.87930	6.93	1.09	7062.44
ε^i(Cont.) = 12.69 cal.deg^{-1}	0.295644	0.263450	0.87770	6.45	1.75	7063.97
ε°(Calor) = 5734.50 ± 0.18 cal.deg^{-1}	0.319137	0.248768	0.87860	6.18	1.38	7064.87
	0.338180	0.240850	0.88654	6.86	1.05	7063.37
				$-\Delta E^\circ_c/M$ = 7062.79 ± 0.64 *		cal.g^{-1}
Propanedithiol-1,3	0.301102	0.245206	0.87737	6.38	2.02	7590.29
M = 108.229	0.307973	0.240751	0.87789	7.41	2.02	7588.17
m^i(Cont.) = 39.28 g	0.316662	0.234803	0.87769	6.19	2.02	7589.23
ε^i(Cont.) = 12.68 cal.deg^{-1}	0.327658	0.227094	0.87748	6.27	1.84	7589.10
ε°(Calor) = 5733.17 ± 0.25 cal.deg^{-1}	0.313254	0.236435	0.87692	6.97	2.02	7591.99
	0.302096	0.245005	0.87817	6.27	2.03	7589.57
	0.297100	0.247847	0.87704	6.61	2.21	7588.39
				$-\Delta E^\circ_c/M$ = 7589.53 ± 0.49 *		cal.g^{-1}
Butanedithiol-1,4	0.366068	0.186837	0.87742	7.87	1.87	7990.21
M = 122.256	0.351432	0.197223	0.87719	7.61	2.03	7993.30
m^i(Cont.) = 39.28 g	0.372327	0.182754	0.87816	5.81	1.78	7996.55
ε^i(Cont.) = 12.65 cal.deg^{-1}	0.358977	0.192181	0.87750	7.96	1.95	7989.73
ε°(Calor) = 5734.50 ± 0.18 cal.deg^{-1}	0.357105	0.194532	0.88030	7.63	1.97	7999.27
	0.339743	0.206967	0.87955	7.12	2.15	7998.81
	0.347161	0.201679	0.87912	7.84	2.08	7989.00
	0.365220	0.191138	0.88404	5.99	1.89	7989.38
	0.351902	0.198965	0.88060	7.15	2.03	7990.46
				$-\Delta E^\circ_c/M$ = 7992.97 ± 1.39 *		cal.g^{-1}
Pentanedithiol-1,5	0.328171	0.211536	0.89037	7.18	2.71	8316.58
M = 136.283	0.347819	0.190724	0.87878	6.83	2.44	8317.08
m^i(Cont.) = 39.29 g	0.317980	0.212987	0.87825	6.66	2.74	8316.91
ε^i(Cont.) = 12.67 cal.deg^{-1}	0.332074	0.203277	0.88037	6.47	2.61	8315.41
ε°(Calor) = 5733.17 ± 0.25 cal.deg^{-1}	0.343615	0.193937	0.87942	7.12	2.50	8317.74
	0.330527	0.204358	0.88005	6.94	2.63	8316.54
				$-\Delta E^\circ_c/M$ = 8316.71 ± 0.32 *		cal.g^{-1}

* The given uncertainties are the standard deviations of mean.

Table 3. Derived data at 25°C.

Compound	ΔE_c° kcal.mole^{-1}	ΔH_c° kcal.mole^{-1}	ΔH_f°(liq) kcal.mole^{-1}	ΔH_v kcal.mole^{-1}	ΔH_f°(gas.) kcal.mole^{-1}
	a)	*a*)	*a*)	*b*)	*a*)
Ethanedithiol-1,2.	—665.33 ± 0.22	—668.00 ± 0.22	—12.91 ± 0.26	10.68 ± 0.03[20]	—2.23 ± 0.26
Propanedithiol-1,3.	—821.41 ± 0.26	—824.37 ± 0.26	—18.90 ± 0.28	11.87 ± 0.03[20]	—7.03 ± 0.28
Butanedithiol-1,4.	—977.19 ± 0.40	—980.45 ± 0.40	—25.20 ± 0.42	13.22 ± 0.09[20] 13.12 ± 0.06[19]	—12.03 ± 0.44
Pentanedithiol-1,5.	—1133.43 ± 0.28	—1136.98 ± 0.28	—31.04 ± 0.30	14.17 ± 0.10[19]	—16.87 ± 0.36

a) The uncertainties in this column are equal to twice the final over-all standard deviation.
b) The uncertainties in this column are the final over-all standard deviations.

$$- m'' \cdot \Delta E_c^\circ/M(\text{Oil}) - m''' \cdot \Delta E_c^\circ/M(\text{Fuse})] - \Delta E_{corr}\} \quad (4)$$

where ΔE_{corr} denotes the sum of items 81—85, 87—91 and 93—94 of the Washburn reduction as given in Ref.[14]

Experimental results. The results of the combustion experiments are summarized in Table 2. The uncertainties given in the table are the standard deviations of the mean. The final over-all precision of the $-\Delta E_c^\circ/M$ mean values was estimated by the method of Bjellerup [15(p. 132)] with one modification to make it applicable to organo-sulphur compounds. The quantity q_5 in these calculations stands for the heat of decomposition of nitric and nitrous acid in the final bomb solution. The ratio s_5/q_5 has been estimated at 0.01.

Derived data. Table 3 gives in the first two columns the values of the standard energies, ΔE_c°, and the standard enthalpies, ΔH_c°, at 25°C calculated according to eqn. 5.

$$\Delta H_c^\circ = \Delta E_c^\circ + \Delta nRT \quad (5)$$

All ΔE_c° and ΔH_c° data refer to the combustion reaction represented by eqn. 1 with all reactants and products in their thermodynamic standard states.

Standard heats of formation, ΔH_f°(liq), at 25°C referring to the reaction represented by eqn. 6

$$n\ \text{C (c, graphite)} + (n+1)\ \text{H}_2\text{(g)} + 2\ \text{S (c, rhombic)} \rightarrow \text{C}_n\text{H}_{2n+2}\text{S}_2\text{(liq)} \quad (6)$$

were calculated by combining the ΔH_c°(liq) values with the standard heats of formation of gaseous carbon dioxide [16], -94.0539 kcal.mole^{-1} *, liquid water [16], -68.3174 kcal.mole^{-1} and sulphuric acid [17] [H_2SO_4, 115 H_2O(liq)], -212.24 ± 0.06 kcal.mole^{-1}.

Heats of vaporization at 25°C have been measured in this laboratory, using two different methods, one applicable in the vapour pressure range 100—1 mm Hg [18], the second in the range $1-10^{-3}$ mm Hg [19]. The results have been included in Table 3 together with the calculated heat of formation data for the compounds in the gaseous state.

DISCUSSION

From the results it is seen that the CH_2-increment in the standard heat of formation values for the gaseous state between consecutive homologues in the series $HS(CH_2)_nSH$, $n = 2-5$, is constant within the limits of error of the measurements, or -4.80, -5.00 and -4.84 kcal.

Further, McCullough has estimated the heats of formation of the compounds from the collected work on thiols, as carried out at the Thermodynamics Laboratory, Bartlesville. A comparison between the experimental and the estimated values is found below. Our experimental values have been recalculated to S_2(g) [1/4 S_8(rhombic) → S_2(g) $\Delta H_{298.16}^\circ = +30.84$ kcal] [22] and a correction has been applied for the difference in heat of formation values for

* This value is corrected to the present atomic weight of 12.011 for carbon.

sulphuric acid between our laboratories; ΔH_f° (H_2SO_4, 115 H_2O) = −212.17 (Bartlesville) and −212.24 (Lund) kcal.mole^{-1}.

ΔH_f°(g)	$n = 2$	3	4	5
Calculated	−32.82	−37.75	−42.68	−47.61
Found	−32.93	−37.73	−42.73	−47.57

It is thus conclusively shown, that the propanedithiol-1,3 falls well within the homologous series and that the experimentally determined values of the strain energy in the dithiolane and dithiane ring systems are not affected by intramolecular interactions between the α and ω thiol groups.

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