

Heats of Combustion and Formation of Thiolane and of the Thiolenes

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The following standard heat of formation values are reported for the compounds in the liquid and gaseous states, at 25°C:

2-thiolene	12.76 and 21.78
3-thiolene	11.31 and 20.86
thiolane	-17.40 and -8.02 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, $\Delta H_f^\circ(\text{H}_2\text{SO}_4, 115 \text{ H}_2\text{O}) = a$. In this case, the published values should be corrected by adding the quantity $(a + 212.24)$ kcal. mole⁻¹.

This investigation was undertaken as a result of a discussion back in 1953 between one of the authors (S.S.) and the late Dr. S. F. Birch of the B. P. Research Centre, Sunbury-on-Thames, who had succeeded in separating and purifying the two dihydrothiophenes (thiolenes) two years earlier¹. The question arose whether the high reactivity of the 2-thiolene over that of its 3-isomer could be traced back, at least in part, to an appreciable difference in strain energy, reflected in a higher heat of formation value for the former isomer.

At the same time it was felt to be within the scope of the investigation to redetermine the heat of combustion of tetrahydrothiophene (thiolane), for which values have been reported by Sunner² in 1949 and by Hubbard, Katz and Waddington³ in 1954. These values are not in agreement and the results of the reinvestigation is, as expected, in close agreement with that of Hubbard *et al.**

Reported values of the heat of combustion of thiophene are in close agreement^{4,5} and a redetermination was therefore not considered necessary.

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*** The heat of combustion value in Ref.² was determined on a sample of only 2.4 g which obviously must have been contaminated somewhere during the last operations.

EXPERIMENTAL

Synthesis and purification of compounds

A 450 g sample of *thiolane* was prepared by reaction of sodium sulphide with 1,4-dichlorobutane according to the method of Lawson, Easley and Wagner⁶. The crude material obtained was first distilled fairly quickly through a 40 cm Vigreux column. It was subsequently refluxed for 1 day over calcium hydride from which it was then fractionally distilled through a 150 cm column packed with glass rings having an efficiency of 25 theoretical plates. Ten equal fractions were collected and each was analysed by V.P.C. (Pye Argon Chromatograph, dioctylphthalate column). The six middle fractions (b.p. 121.11–121.12°C at 760 mm Hg) were judged to be of equally high purity and were combined and then further dried over silica gel and finally over calcium sulphate. The sample used for combustion studies was distilled *in vacuo* from calcium sulphate. Part of the combustion sample was contaminated with 0.05 mole % thiophene and V.P.C. analysis of this material gave a chromatogram with an easily detectable thiophene peak. Absence of any similar impurity peaks in the chromatogram of the combustion sample established the purity of this sample at > 99.95 mole %. The densities and refractive indices at 20 and 25°C and the melting point of the combustion sample were measured and these properties, together with the boiling point and estimated purity, are listed in Table 1.

Samples of *2-thiolene* and *3-thiolene* were supplied by the B.P. Research Centre, Sunbury-on-Thames, Middlesex, England. Further samples were prepared as described by Birch and McAllan¹ by the reduction of thiophene with sodium in a medium of liquid ammonia. Three syntheses yielded 110 g of 2-thiolene and 150 g of 3-thiolene in fairly high purity, as indicated by analysis with the Pye chromatograph (dioctylphthalate column). Care had to be taken in handling these compounds in view of their unstable nature. This was particularly so with the 2-isomer which polymerizes rapidly when brought into contact with air. Consequently, whenever possible, the compounds were handled in an atmosphere of dry nitrogen and stored in a refrigerator at –20°C.

After drying over calcium sulphate for 2 days the 2-thiolene was further purified by careful fractional distillation through the 150 cm column mentioned above in an

Table 1. Comparison with earlier data of the physical properties of the samples prepared in the present investigation.

Compound and reference	Density g/ml		Refractive index		Melting point for zero impurity (°C)	Boiling point (°C)	Estimated purity mole %
	20°C	25°C	n_D^{20}	n_D^{25}			
Thiolane A.P.I. Research Project 44 This work	0.99869 0.9988 ± 0.0002	0.99379 0.9939 ± 0.0002	1.50483 1.5049 ± 0.0002	1.50217 1.5022 ± 0.0002	–96.16 –96.8 ± 1.0	121.12 (760 mm) 121.11–121.12 (760 mm)	> 99.95
2-Thiolene Birch and McAllan ⁴ This work	1.0361 1.0391 ± 0.0002	1.0340 1.0340 ± 0.0002	1.5311 1.5301 ± 0.0002	1.5276 1.5276 ± 0.0002	–108.7 –109.6 ± 1.0	112.0 (760 mm) 64.8–65.0 (160 mm)	97.5 99.86
3-Thiolene Birch and McAllan ⁴ This work	1.0591 1.0589 ± 0.0002	1.0536 1.0536 ± 0.0002	1.5306 1.5298 ± 0.0002	1.5274 1.5274 ± 0.0002	–49.3 –50.1 ± 1.0	122.3 (760 mm) 76.2–76.3 (185 mm)	98.5 > 99.88

atmosphere of dry nitrogen at 160 mm Hg. Four equal fractions were collected and chromatographed. Fractions II and III (b.p. 64.8–65.0°C at 160 mm Hg) were selected. After drying over calcium sulphate in a nitrogen atmosphere for 2 days this material was finally distilled *in vacuo* from calcium sulphate to provide the sample used for combustion studies. The physical properties of this sample are given in Table 1. Chromatographic analysis indicated the presence of a small amount of thiophene in the sample. This was estimated at 0.15 ± 0.07 mole % by contaminating part of the sample with a further 0.50 mole % thiophene and chromatographing this mixture and the purest sample under identical conditions. From the different areas under the thiophene peaks in the two chromatograms the percentage of thiophene in the purest sample was estimated. A repeat of this procedure checked the accuracy of the estimation. The chromatograms indicated the absence of any other impurity.

The 3-thiolene was further purified by careful fractionation through the 150 cm column in an atmosphere of dry nitrogen at 80 mm Hg. The purest fractions were selected by gas chromatographic analysis (dioctylphthalate column) and these were re-distilled twice in an atmosphere of dry nitrogen through a 75 cm column packed with glass helices. The purest fraction from the final distillation (b.p. 76.2–76.3°C at 185 mm Hg) was selected by V.P.C. analysis and this was then dried for 4 days in a nitrogen atmosphere over calcium sulphate from which it was then distilled *in vacuo*. Combustion studies and measurements of physical properties were made on this distillate. The physical properties are to be found in Table 1. Analysis with the Pye chromatograph, carried out in the manner described above, indicated the presence of 0.07 ± 0.04 mole% of thiophene in this sample. This analysis also indicated that the sample contained < 0.05 mole% 2-thiolene, which was the only other impurity.

Heat of combustion measurements

Apparatus and procedure. The rotating-bomb calorimeter system used was that of Bjellerup⁷ and the combustion procedure of Sunner and Lundin⁸ was followed. Concerning further details reference is made to the preceding paper⁹.

Materials. The benzoic acid used in the calibration experiments was National Bureau of Standards standard sample 39h¹⁰. The paraffin oil used as auxiliary material was sample USBM-P3a, described in Ref.⁷ (p. 1531).

The compounds were sealed in thin glass ampoules which were filled by distilling the combustion sample *in vacuo* into a receiver containing the ampoules and then admitting a small pressure of dry nitrogen, so causing the ampoules to fill. With the 2-thiolene, even though the ampoules were dried in stream of dry nitrogen, they became coated with a film of polymeric material. This was removed by carefully cleaning the ampoules with concentrated nitric acid and then washing them with distilled water and acetone. No such difficulty was encountered with the other two compounds.

Some experiments were unsuccessful because of formation of sulphur dioxide which could often be smelt in the bomb gases after the combustion. Sulphur dioxide formation was also accompanied by the total absence of nitrous acid in the bomb solution and experiments in which no nitrous acid was formed were rejected.

Small corrections were made for the formation of significant quantities of carbon in experiments 2 and 3 on 2-thiolene. The measured heats of combustion of 2-thiolene and 3-thiolene were corrected for the presence of thiophene in the combustion samples using the value for the heat of combustion of thiophene $\Delta H_c^\circ = -675.88$ kcal/mole, reported by Sunner⁴. No correction was made for the 2-thiolene content (< 0.05 mole%) of the 3-thiolene sample.

Units. Auxiliary quantities. Calculation of results. Heats of combustion and formation are given in thermochemical calories, defined by 1 cal = 4.1840 abs. joules and refer to the isothermal process at 25°C and to the true mass. The molecular weights were computed from the 1957 table of atomic weights¹¹. The $-\Delta E_c^\circ/M$ values refer to reaction (1) in which all reactants and products are in their thermodynamic standard states:

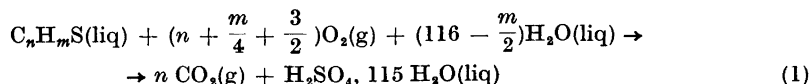


Table 2. Results of combustion experiments.

$t_h = 25.0^\circ\text{C}$	$\varepsilon^\circ(\text{Calor}) = 5732.39 \pm 0.42 \text{ cal deg}^{-1}$
$t_i = 24.1^\circ\text{C}$	$\varepsilon^i(\text{Cont.}) = 12.61 - 12.62 \text{ cal deg}^{-1}$
$P_i(\text{gas.}) = 30.0 \text{ atm.}$	$m(\text{Pt}) = 18.585 - 18.621 \text{ g}$
$V(\text{Bomb}) = 0.2628 \text{ liter}$	$m''' = 0.003548 - 0.004808 \text{ g}$
$V^i(\text{soln.}) = 0.01002 \text{ liter}$	$m(\text{glass}) = 0.0491 - 0.1061 \text{ g}$
$V^i(\text{gas.}) = 0.2522 \text{ liter}$	

m' g	m'' g	Δt deg	$\Delta E_{\text{dec.}}^f(\text{HNO}_3 + \text{HNO}_2)$ cal	$\Delta E_{\text{corr.}}$ cal	$-\Delta E_c^\circ/M$ cal g ⁻¹
2-Thiolene					
0.456391	0.100425	0.88075	4.05	2.87	8542.92
0.431597	0.116093	0.87363	3.91	3.03	8540.63
0.432569	0.118540	0.88009	5.29	3.03	8541.62
0.476043	0.085173	0.88100	7.26	2.74	8541.43
0.438338	0.114194	0.88086	7.89	2.99	8545.12
				Mean	8542.34
				Standard deviation of mean	± 0.79
3-Thiolene					
0.480960	0.079493	0.87667	5.58	2.68	8528.69
0.475387	0.084467	0.87783	8.70	2.72	8524.95
0.457623	0.098802	0.87868	7.28	2.85	8527.28
0.476165	0.084004	0.87779	7.22	2.71	8527.86
0.483864	0.078562	0.87906	8.36	2.66	8527.60
0.460961	0.095843	0.87715	3.72	2.82	8523.45
0.476793	0.084023	0.87785	4.93	2.71	8523.89
0.468057	0.089835	0.87723	8.74	2.77	8526.91
0.477281	0.083287	0.87700	3.68	2.70	8522.34
				Mean	8525.89
				Standard deviation of mean	± 0.73
Thiolane					
0.452198	0.092219	0.87825	8.93	2.57	8775.85
0.425799	0.113271	0.87795	7.01	2.76	8778.74
0.455119	0.089705	0.87660	1.44	2.55	8775.99
0.467342	0.080231	0.87810	6.19	2.46	8779.39
0.433748	0.106491	0.87768	9.28	2.71	8777.08
				Mean	8777.41
				Standard deviation of mean	± 0.72

In calibration experiments the certified value for the heat of combustion of the benzoic acid under certificate conditions, $-\Delta E_c/M = 6317.88 \pm 0.72 \text{ cal.g}^{-1}$, was used. The standard heats of combustion were, for paraffin oil USBM-P3a and for the fuse $-\Delta E_c/M = 10984.1 \pm 1.8$ and $3971 \pm 4 \text{ cal.g}^{-1}$, respectively.

The results of the combustion experiments were calculated according to Hubbard, Scott and Waddington¹² and Bjellerup, *cf.* Ref.⁹

Experimental results. The results of the combustion experiments are summarized in Table 2. The symbols have the meanings given in Refs.^{9,12} The uncertainties given are the standard deviations of the mean.

Derived data. Table 3 gives the values of the standard energies, ΔE_c° , and the standard enthalpies, ΔH_c° , at 25°C . All values refer to the combustion reaction represented by eqn. (1).

Table 3. Derived data at 25°C.^a

Compound	ΔE_c° kcal.mole ⁻¹	ΔH_c° kcal.mole ⁻¹	$\Delta H_f^\circ(\text{liq})$ kcal.mole ⁻¹	ΔH_v kcal.mole ⁻¹	$\Delta H_f^\circ(\text{g})$ kcal.mole ⁻¹
2-Thiolene	735.99 ± 0.25	737.85 ± 0.25 ^b	12.76 ± 0.28	9.02 ± 0.10	21.78 ± 0.30
3-Thiolene	734.57 ± 0.25	736.40 ± 0.25 ^b	11.31 ± 0.28	9.55 ± 0.06	20.86 ± 0.28
Thiolane	773.94 ± 0.25	776.01 ± 0.25	-17.40 ± 0.28 ^c	9.38 ± 0.06 ^c	-8.02 ± 0.28 ^c

a) All uncertainties are twice the final over-all standard deviation.

b) After correction for thiophene content.

c) Ref.³ gives the value = -17.31 ± 0.35 kcal.mole⁻¹, recalculated to the atomic weight of carbon 12.011 and the heat of formation value for sulfuric acid, H₂SO₄, 115 H₂O, $\Delta H_f^\circ = -212.24$ kcal.mole⁻¹ used in this investigation, it becomes = -17.37 kcal.mole⁻¹. The heat of vaporization at 25°C given in Ref.³ is 9.23 kcal.mole⁻¹, and thus $\Delta H_f^\circ(\text{g})$ becomes -8.14 ± 0.35 kcal.mole⁻¹.

The final over-all precision of the mean values was estimated by the method of Bjellerup¹³. They include allowances for the error in the measurements of the thiophene content of the samples. Standard heats of formation, $\Delta H_f^\circ(\text{liq})$, at 25°C were calculated using the standard heats of formation of gaseous carbon dioxide¹⁴, liquid water¹⁴ and sulphuric acid¹⁵ [H₂SO₄, 115 H₂O] -94.0539, -68.3174 and -212.24 ± 0.06 kcal.mole⁻¹, respectively.

The heats of vaporization at 25°C were measured in this laboratory¹⁶ using the apparatus described by Wadsö¹⁷. They have been included in Table 3 together with heat of formation data for the compounds in the gaseous state.

DISCUSSION

The heat of formation values for the two dithiolenes are only 0.9 kcal.mole⁻¹ apart. The 2-isomer has the highest energy, although it should be stabilized due to conjugation between the C=C double bond and the sulphur atom. Unfortunately, no thermochemical data are available for the estimation of the resonance energy of the C=C-S moiety. However, vinyl ethyl ether

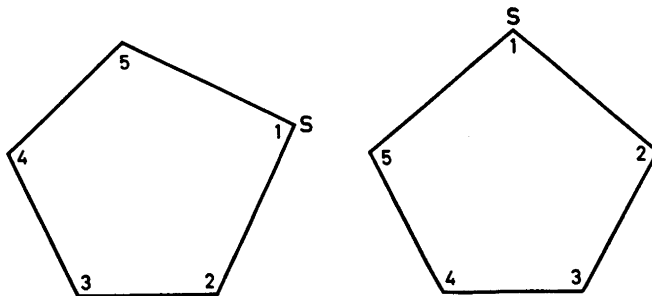


Fig. 1. The ring structure of

- a) 2-thiolene (angle 1 equals 93°, 2 = 3 equal 115°, 4 = 5 equal 108–109°) and
 b) 3-thiolene (angle 1 equals 98°, 2 = 5 equal 104°, 3 = 4 equal 117°).

and divinyl ether both show a resonance energy of *ca.* 3.5 kcal.mole⁻¹ (Ref.¹⁸, p. 85) and the corresponding figure for the sulphur analogues should be less than that. Thus, the 2-thiolene seems to have a strain energy of about 3 to 4 kcal in excess of that of 3-thiolene.

The calculated heat of hydrogenation of 3-thiolene is $\Delta H_h = -28.9$ kcal.mole⁻¹ which, within the limits of error, is the same as the heat of hydrogenation of *cis*-2-butene, -28.6 kcal.mole⁻¹. The strain energy of this isomer is therefore about the same as it is in thiolane. Using the revised value for the heat of formation of this compound its strain energy is estimated at 1.5–2 kcal.mole⁻¹ according to the procedure described in Ref.² Thus, the strain energy of 3-thiolene is *ca.* 2 kcal.mole⁻¹ whereas that of the 2-isomer *minus* its resonance energy is *ca.* 3 kcal.mole⁻¹.

A structural analysis is also in qualitative agreement with the above results. Taking reasonable values for the lengths of the various bonds in the two isomers¹⁹ and assuming a coplanar ring structure, models of the two isomers can be constructed (Fig. 1) in which the angle strain is approximately minimized when compared with reasonable values of the bond angles in open chain molecules. Assuming normal bond angle values of 120° for C=C–X, 105° for C–S–C and 109.5° for C–C–X, X=C or S, it is seen that in order to obtain a ring the angles have to be compressed altogether by 24°. In 3-thiolene the distortions can be rather evenly distributed between the five ring angles, whereas in the 2-isomer the C=C–X and particularly the C–S–C angles have to take the whole angle compression. A more equal distribution leads to an expansion of the two C–C–X angles towards 109.5° and a considerable increase in the sum of the squares of the angle distortion, which is roughly proportional to the angle strain energy. The indication is that the angle strain in the 2-thiolene should be *ca.* 1.7 times that in the 3-isomer. In addition, the 2-isomer possesses two adjacent methylene groups in the eclipsed position which should increase its strain by at least 1 kcal.mole⁻¹.

It does not seem likely, that the rather small ring strain in 2-thiolene could bring about the high reactivity of this isomer. It is undoubtedly more easily explained as a result of the presence of the C=C–S vinyl system.

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