measurable, this is not the case when verification of the correctness of the spreading pressures is considered. The meaning of spreading pressures has been discussed recently by Everett[39] and by Pierce and Smith.[40] Everett considers that although spreading pressures measured on liquids have a perfectly definite meaning, this is not the case for solids where he considers that the physical interpretation of spreading pressures is uncertain. Pierce and Smith consider that for an energetically heterogeneous surface, such as that used in this work, the computation of spreading pressures from isotherms may be misleading. As well as the assumptions involved in the calculation of the surface energy lowering, there is the additional assumption, which has to be made in order to relate the expansion to the elastic constants, that the surface energy lowering is equal to the surface tension lowering. Shuttleworth[41] has emphasized that for solids the absolute value of the surface energy and surface tension may be very different, but he has not considered changes in these quantities. Bangham[18] has shown that in the particular type of physical adsorption in which the adsorbed molecules behave as a two-dimensional gas the surface tension and energy lowering are equal, but he did not consider the case in which molecular mobility takes place by a series of short jumps over the surface during the time of adsorption. For non-uniform surfaces the latter mechanism has been suggested by Tompkins[42] and de Boer.[43]

One factor of importance in this work is that it shows that adsorbate–adsorbent interaction causes perturbation of the adsorbent.[44,45] This perturbation has often been assumed negligible in theoretical treatments,[22,39,46] and in experimental work using the assumption that the thermodynamic properties of the adsorbed gas are those of a one-component system.[47] If the perturbation of the adsorbent were negligible, it would be expected that no size changes would occur in the adsorbent on adsorption. The fact that size changes do occur, even if small in magnitude, makes the assumption of an inert adsorbent, for physical adsorption, of very doubtful validity.

When adsorption takes place the environment and thus the chemical potential of the surface lattice elements changes; in order to maintain homogeneity in the chemical potential the surroundings of internal lattice elements must change also. These changes result in the swelling of an ionic solid when non-polar gases are adsorbed and in the contraction of the solid when small quantities of certain polar gases are adsorbed, followed by a swelling at higher adsorptions.

The author wishes to thank the Corning Glass Company, of Corning, New York, for the gift of the porous glass used in this work and for information concerning its properties.

Thanks are due to Dr. J. H. Schulman, O.B.E., for helpful discussions and advice. The author wishes to acknowledge the support of the Consolidated Zinc Corporation in the early phases of this work and of the Council of the British Ceramic Research Association in the concluding phases.

---

[39] D. H. Everett, *Trans. Faraday Soc.*, **46**, 942 (1950).

[40] C. Pierce and R. N. Smith, *J. Am. Chem. Soc.*, **75**, 846 (1953).

[41] R. Shuttleworth, *Proc. Phys. Soc.*, **A63**, 444 (1950).

[42] F. C. Tompkins, *Trans. Faraday Soc.*, **46**, 569 (1950).

[43] J. H. de Boer, "The Dynamical Character of Adsorption," Oxford University Press, London, 1953.

[44] M. A. Cook, D. H. Pack and A. G. Oblad, *J. Chem. Phys.*, **19**, 367 (1951).

[45] S. Brunauer, "Structure and Properties of Solid Surfaces," University of Chicago Press, Chicago, 1953, p. 395.

[46] T. L. Hill, *Trans. Faraday Soc.*, **47**, 376 (1951).

[47] L. E. Drain and J. A. Morrison, *ibid.*, **48**, 840 (1952).

PURIFICATION AND PROPERTIES OF TEN ORGANIC SULFUR COMPOUNDS—SECOND SERIES[1]

BY WILLIAM E. HAINES, R. VERNON HELM, GLENN L. COOK AND JOHN S. BALL

Bureau of Mines, Petroleum and Oil-Shale Experiment Station, Laramie, Wyoming

Received July 18, 1955

Ten organic sulfur compounds, 2-propanethiol, 1-butanethiol, 2-butanethiol, 2-thiapropane, 2-thiapentane, 3-methyl-2-thiabutane, thiacyclohexane, 2-methylthiophene, 3-methylthiophene and benzo[b]thiophene, were purified to at least 99.9 mole % purity. In addition to the boiling point, freezing point and cryoscopic constant, the following properties were measured at 20, 25 and 30°: density, viscosity, surface tension and refractive index for the r, C, D, e, v, F, and g lines. Derived functions, including refractivity intercept, specific dispersion, molecular refraction, parachor and molecular volume, were calculated. Mass, infrared and ultraviolet spectra were determined, permitting some correlation of the effect of sulfur groupings on spectra. The stability of the compounds under storage conditions was investigated.

One of the aims of American Petroleum Institute Research Project 48A, which is coöperatively sponsored by the Bureau of Mines and the API, is to supply fundamental data concerning sulfur compounds that occur in petroleum. High-purity thiols, sulfides, disulfides and thiophenes are prepared so that three groups of physical properties can be determined accurately: (1) common physical properties, including refractive index, density, viscosity, surface tension, melting point, cryoscopic constant and boiling point; (2) reference spectra; and (3) thermodynamic properties. The properties of the first series of ten compounds, including ethanethiol, 2-methyl-2-propanethiol, 1-pentanethiol, 2-thiabutane, 3-thiapentane, thiacyclobutane, thiacyclopentane, 2,3-dithiabutane,

---

[1] This investigation was performed as part of the work of American Petroleum Institute Research Project 48A on "The Production, Isolation, and Purification of Sulfur Compounds and Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

3,4-dithiahexane, and thiophene, were reported previously.[2] This paper reports the common physical properties and spectra of the second series of ten sulfur compounds. Other investigators recently have reported values for several of these properties.[3] The thermodynamic properties of some of these compounds have been reported in separate papers.[4]

A sufficient quantity of each compound is prepared to facilitate the attainment of high purity and to assure an adequate supply for the measurement of properties. A small surplus of each compound usually results and this material is made available to the industry as calibration standards through the API Samples and Data Office at Carnegie Institute of Technology. Because of their use as calibration standards, the storage stabilities of the compounds have been investigated.

The compounds included in the present study, together with their common names and sample numbers, are shown below

Thiols		
2-Propanethiol	Isopropyl mercaptan	API-USBM 11-5S
1-Butanethiol	*n*-Butyl mercaptan	API-USBM 14-5S
2-Butanethiol	*sec*-Butyl mercaptan	API-USBM 19-5S
Sulfides		
2-Thiapropane	Dimethyl sulfide	API-USBM 13-5S
2-Thiapentane	Methyl *n*-propyl sulfide	API-USBM 18-5S
3-Methyl-2-thiabutane	Methyl isopropyl sulfide	API-USBM 20-5S
Cyclic sulfide		
Thiacyclohexane	Pentamethylene sulfide	API-USBM 17-5S
Thiophenes		
2-Methylthiophene		API-USBM 16-5S
3-Methylthiophene		API-USBM 12-5S
Benzo[b]thiophene	Thianaphthene	API-USBM 15-5S

Purification.—To meet the needs of the program, approximately 1.5 liters of material with a purity of at least 99.9 mole % was required. The purification procedures used were similar to those described in the previous paper[2] in which choice of fractions and of methods was guided by freezing point purity measurements. Details of the purification procedures used for individual compounds are described below. All distillations were made at atmospheric pressure (585 mm.) unless otherwise noted.

2-Propanethiol.—The raw material consisted of 2.5 l. purchased from Eastman Kodak Company plus 1.5 l. of material that had been recovered from a caustic wash of petroleum naphtha by the Union Oil Company of California. This sample was distilled through a 1-inch by 9-foot column packed with stainless-steel helices (hereinafter designated as column 1). The yield of high-purity (99.98 mole %) material was 1.6 l.

1-Butanethiol.—Approximately 4 l. of material purchased from Eastman Kodak Company was distilled through column 1. The yield of high purity (99.96 mole %) material was 1.5 l.

2-Butanethiol.—Four liters of material, synthesized and given to the Project by California Research Corporation, was distilled through a 1-inch by 8-foot Oldershaw column (column 2). It was impossible to follow the purification by the freezing point method because the compound formed a glass when cooled. A portion of the distillate, estimated to have a purity of 99.9 mole %, was therefore chosen by comparing the mass spectra of the various fractions. A sample of this selected material was submitted to the Thermodynamics Laboratory, Bureau of Mines, Bartlesville, Oklahoma, for determination of purity. The sample failed to crystallize, even under the conditions in the low temperature cryostat, although a sample of less purity (99.7 mole %) had given satisfactory results. Final purity was therefore estimated by mass spectrometry, utilizing the mass spectra of the less pure sample for comparison. The yield of high purity (99.9 mole %) material was 1.5 l.

2-Thiapropane.—Four liters of material purchased from Eastman Kodak Company was dried over anhydrous calcium sulfate and charged to a high temperature Podbielniak heligrid column with a 5-foot packed section (column 3). Approximately 3 l. of pure material (99.99 mole %) was recovered.

2-Thiapentane.—This compound was synthesized by a method based on suggestions of Bordwell and Kern.[5] Three moles of *n*-propyl bromide was added dropwise to 3 moles of sodium methyl mercaptide prepared by dissolving methanethiol in 10% sodium hydroxide. Stirring was continued for 45 minutes after addition was completed, and the mixture was then refluxed for 2 hours. The product was recovered by steam distillation and washed successively with 5% sodium hydroxide, 5% hydrochloric acid and distilled water. Twenty batches were prepared, with an average yield of 93 mole %. The methanethiol used in this and the succeeding synthesis was donated to the Project by Union Oil Company of California. The crude 2-thiapentane thus prepared (5.6 l.) was dried over anhydrous potassium carbonate and distilled through column 2. The yield of high purity (99.97 mole %) material was 2.0 l.

3-Methyl-2-thiabutane.—This compound was synthesized using isopropyl bromide in place of *n*-propyl bromide in the above procedure. Reflux time was extended to 4 hours. The steam distilled product contained about 15% of unreacted bromide. Correcting for this bromide, the average yield for the 26 3-mole batches was 81% of theoretical. The crude sulfide (7.6 l.) was distilled through a 6-foot Stedman-packed column 1 inch in diameter (column 4). The yield of high-purity (99.99 mole %) material was 3.3 l.

Thiacyclohexane.—This compound was prepared by a method based on the general suggestions of Bordwell and Pitt.[6] A solution of 486 g. of sodium sulfide (60% fused chips) in 500 ml. of water was refluxed and stirred vigorously while 405 ml. (3 moles) of 1,5-dibromopentane was added. This addition was made dropwise over a period of 2 hours. Stirring and reflux were continued for an additional 4 hours. The product was then steam distilled from the reaction mixture, washed with 5% sodium chloride solution and dried over anhydrous potassium carbonate. The yield of crude thiacyclohexane was 71% of theoretical. Four liters of the crude product was distilled through column 4, yielding 2.0 l. of high purity (99.94 mole %) material.

2-Methylthiophene.—Approximately 3.3 liters of 2-methylthiophene furnished by Socony-Mobil Oil Company was distilled in column 3, yielding 0.8 l. of material with a purity

---

(2) W. E. Haines, R. V. Helm, C. W. Bailey and J. S. Ball, THIS JOURNAL, **58**, 270 (1954).

(3) D. H. Desty and F. A. Fidler, *Ind. Eng. Chem.*, **43**, 905 (1951); R. L. Denyer, F. A. Fidler and R. A. Lowry, *ibid.*, **41**, 2727 (1949); F. S. Fawcett, *J. Am. Chem. Soc.*, **68**, 1420 (1946); S. Mathias, *ibid.*, **72**, 1897 (1950); D. T. McAllan, T. V. Cullum, R. A. Dean and F. A. Fidler, *ibid.*, **73**, 3627 (1951); S. Sunner, Thesis, University of Lund, Sweden, 1950; A. I. Vogel, *J. Chem. Soc.*, 1820 (1948); P. T. White, D. G. Barnard-Smith and F. A. Fidler, *Ind. Eng. Chem.*, **44**, 1430 (1952).

(4) J. P. McCullough, S. Sunner, H. L. Finke, W. N. Hubbard, M. E. Gross, R. E. Pennington, J. F. Messerly, W. D. Good and Guy Waddington, *J. Am. Chem. Soc.*, **75**, 5075 (1953); H. L. Finke, M. E. Gross, J. F. Messerly and Guy Waddington, *ibid.*, **76**, 854 (1954); J. P. McCullough, H. L. Finke, W. N. Hubbard, W. D. Good, R. E. Pennington, J. F. Messerly and Guy Waddington, *ibid.*, **76**, 2661 (1954); J. P. McCullough, H. L. Finke, D. W. Scott, M. E. Gross, J. F. Messerly, R. E. Pennington and Guy Waddington, *ibid.*, **76**, 4796 (1954).

(5) F. G. Bordwell and R. J. Kern, communication from API Project 48B at Northwestern University.

(6) F. G. Bordwell and B. M. Pitt, communication from API Project 48B at Northwestern University.

of 99.8 mole %.[7] The shoulder fractions from this distillation were combined with 3 l. of additional raw material for distillation in column 1. Fractions from this distillation were combined to yield 2 l. of material with a purity of 99.5 mole %. The latter sample plus the 0.8 l. from the first distillation were combined and distilled through column 2, yielding 1.1 l. of high purity (99.96 mole %) material.

3-Methylthiophene.—Three liters of 3-methylthiophene furnished by Socony-Mobil Oil Company was distilled through column 1, yielding 2 l. of material with a purity of 99.9 mole %. This sample discolored after standing several weeks and later deposited a dark red-brown film on the storage bottles so that a distillation through column 2 and additional purity measurements were made just before bottling *in vacuo*. The yield of high-purity (99.97 mole %) material was 1.4 l.

Benzo[b]thiophene.—Two separate 2-l. batches of material given to the Project by The Texas Company were distilled through column 4 at a pressure of 50 mm. The highest purity fractions from each of these distillations were combined and redistilled in the same column at a pressure of 90 mm. yielding 1.5 l. of high purity (99.97 mole %) material. Because ordinary freezing-point purity measurements gave poor precision, the purity of the final sample was measured by the Thermodynamics Laboratory.

Stability.—Inasmuch as a portion of each of these compounds has been set aside as a calibration standard, the storage stability was of considerable interest. This stability was estimated by an "accelerated" test in the following manner. Samples of the purified compounds were sealed *in vacuo* and exposed to sunlight on the laboratory roof for one year. Control samples were kept in the dark during the same period. Determinations of purity by the freezing point method were made on both the exposed and control samples.

None of the control samples showed any detectable decrease in purity. Five of the samples—2-propanethiol, 1-butanethiol, 2-thiapentane, 3-methyl-2-thiabutane and thiacyclohexane—were unaffected by storage in the sunlight. Two samples having high vapor pressure—2-butanethiol and 2-thiapropane—exploded during the summer months and data on replacements are not yet available.

The two alkyl thiophenes showed different degrees of decomposition after storage in the sunlight. The 2-methylthiophene had a light-straw color and showed a freezing point purity of 99.93 mole %, 0.03 mole % lower than the control sample. The 3-methylthiophene was yellow and had decreased in purity 0.08 mole %.

A marked and interesting decomposition was shown by the benzo[b]thiophene. A 50-ml. sample, sealed *in vacuo*, was found, after 6 months' exposure, to have exploded violently. As the vapor pressure of this solid compound is only 25 mm. at 100°, the explosion cannot be explained on this basis. A 5-ml. breakoff-tip ampoule was exposed for 1 year without incident. The color of this sample had changed from white to red-brown. Because the experience with the first sample suggested that a gas had been formed, the second sample was opened directly into the mass spectrometer to determine what gas, if any, was present. The mass spectrum thus obtained showed large concentrations of hydrogen sulfide and small amounts of hydrogen in the gas above the solid sample. Insufficient sample was available for rigorous freezing point purity determination, but a rough measurement showed a decrease in freezing point of 1.8°.

A mass spectrum of the decomposed solid was obtained using an instrument equipped for high mass work. Significant peaks at *m/e* 234 and *m/e* 266, considerably above the parent peak at *m/e* 134, were observed.

An ultraviolet spectrum on the exposed sample differed from that of the control as shown in Fig. 1. The increased long wave length absorption suggests condensation of the molecules.

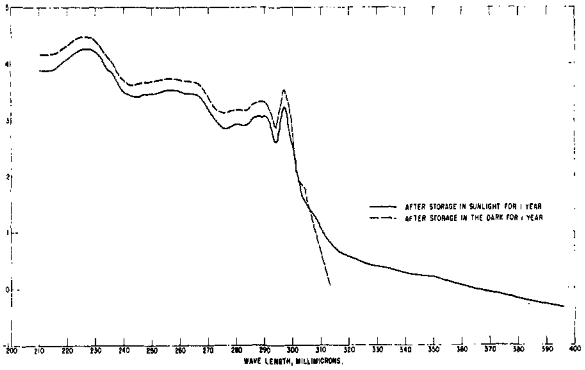
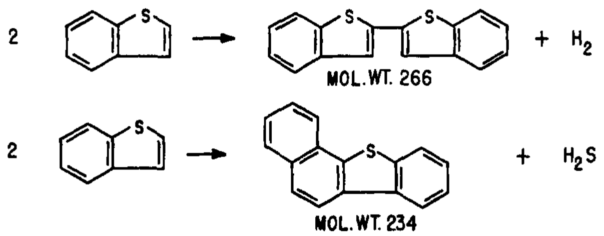


Fig. 1.—Ultraviolet spectra of benzo[b]thiophene.

A mechanism that fits the above data is postulated



Physical Properties.—Physical property data for the ten organic sulfur compounds are shown in Tables I and II. Apparatus and procedures used for the first nine compounds were the same as those described in detail in a previous paper.[2] The following accuracy of each of the measurements was estimated: freezing point, ±0.01°; boiling point, ±0.1°; refractive index, ±0.00006; density, ±0.00005 g./ml.; viscosity, ±0.001 centipoise; and surface tension, ±0.1 dyne/cm.

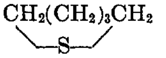
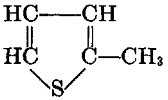
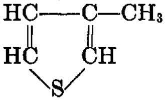
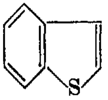
Some modifications in techniques were necessary to determine the physical properties of benzo[b]thiophene. This material has a high dispersion and a melting point above the temperatures at which properties are normally measured. Refractive index was measured with an Abbe refractometer having compensating prisms, and density was determined by means of calibrated pycnometers. Uncertainties for the benzothiophene values reported are: refractive index, ±0.0001; density, ±0.0001 g./ml.; viscosity, ±0.003 centipoise; surface tension, ±0.3 dyne/cm. Estimated accuracies for the freezing point and boiling point are as previously stated.

---

[7] As toluene was one of the impurities, invalidation of freezing point purity results would be expected if toluene formed a solid solution with 2-methylthiophene similar to the solid solution formed by benzene and thiophene. Experiments made by adding toluene to the methylthiophene showed no solid solution of these two compounds.

TABLE I

REFRACTIVE INDICES OF TEN ORGANIC SULFUR COMPOUNDS

Cpd. no.	Compound	Temp. of measurement, t, °C.	Refractive indices, n^t						
			Helium r line 6678.1 Å.	Hydrogen C line 6562.8 Å.	Sodium D line 5892.6 Å.	Mercury e line 5460.7 Å.	Helium v line 5015.7 Å.	Hydrogen F line 4861.3 Å.	Mercury g line 4358.3 Å.
1	$CH_3CHSHCH_3$	20	1.42236	1.42277	1.42554	1.42795	1.43110	1.43248	1.43802
		25	1.41938	1.41978	1.42251	1.42487	1.42802	1.42929	1.43487
		30	1.41613	1.41660	1.41927	1.42163	1.42479	1.42611	1.43156
2	$CH_3(CH_2)_3SH$	20	1.43976	1.44022	1.44298	1.44535	1.44845	1.44982	1.45529
		25	1.43715	1.43758	1.44034	1.44270	1.44582	1.44718	1.45255
		30	1.43433	1.43475	1.43750	1.43982	1.44289	1.44422	1.44962
3	$CH_3CHSHCH_2CH_3$	20	1.43350	1.43399	1.43673	1.43909	1.44219	1.44344	1.44892
		25	1.43081	1.43123	1.43396	1.43632	1.43938	1.44062	1.44607
		30	1.42808	1.42848	1.43114	1.43345	1.43656	1.43786	1.44319
4	CH_3SCH_3	20	1.43198	1.43249	1.43547	1.43798	1.44136	1.44286	1.44883
		25	1.42893	1.42938	1.43231	1.43481	1.43820	1.43957	1.44557
		30	1.42562	1.42607	1.42900	1.43145	1.43485	1.43625	1.44208
5	$CH_3S(CH_2)_2CH_3$	20	1.44111	1.44158	1.44435	1.44674	1.44993	1.45129	1.45686
		25	1.43841	1.43884	1.44163	1.44400	1.44716	1.44847	1.45402
		30	1.43569	1.43609	1.43888	1.44121	1.44436	1.44567	1.45117
6	$CH_3SCH(CH_3)_2$	20	1.43588	1.43631	1.43914	1.44155	1.44475	1.44608	1.45170
		25	1.43308	1.43359	1.43634	1.43871	1.44195	1.44322	1.44879
		30	1.43033	1.43075	1.43354	1.43586	1.43904	1.44031	1.44588
7		20	1.50309	1.50358	1.50684	1.50958	1.51331	1.51484	1.52132
		25	1.50055	1.50107	1.50426	1.50704	1.51068	1.51223	1.51867
		30	1.49801	1.49850	1.50173	1.50447	1.50811	1.50959	1.51604
8		20	1.51502	1.51570	1.52035	1.52440	1.52985	1.53218	1.54212
		25	1.51218	1.51283	1.51744	1.52145	1.52685	1.52918	1.53907
		30	1.50923	1.50988	1.51451	1.51847	1.52384	1.52615	1.53598
9		20	1.51518	1.51585	1.52042	1.52440	1.52984	1.53210	1.54181
		25	1.51241	1.51300	1.51758	1.52153	1.52688	1.52913	1.53885
		30	1.50943	1.51008	1.51455	1.51851	1.52390	1.52612	1.53572
10		35			1.6332				
		40			1.6302				

Derived Functions.—Two types of derived functions have been calculated using the physical property data. Specific dispersion and refractivity intercept, used analytically to distinguish different classes of hydrocarbons, are functions of the non-additive type. The additive or constitutive functions are molecular volume, molecular refraction and parachor. All functions shown in Table III are calculated at 20°. For benzothiophene, properties at 20° were estimated by extrapolation from 35 and 40° properties.

The refractivity intercepts of the sulfur compounds are generally lower than those of the similar hydrocarbons, and consequently sulfur impurities will cause high values in the estimation of cycloparaffins using this function.

Specific dispersion has been used to estimate the aromatic content of oils because of the large difference in the specific dispersion of the paraffin hydrocarbons (about 98) and the aromatics (around 185). Table III shows that the sulfur compounds fall between these values, and thus the presence of sulfur compounds as impurities would cause high values in the estimation of aromatics by specific dispersion.

Molecular refractions, molecular volumes and parachors are shown in Table III. In compliance with the current practice, the molecular volumes are at 20° rather than at the boiling point, as in the previous paper. Quite satisfactory formulas for calculating these functions for hydrocarbons are available and it would be convenient if an increment for sulfur could simply be added to these equations. However, no such simple relationship was found and insufficient data are as yet available to study the various types of sulfur compounds.

Spectra.—Mass, ultraviolet and infrared spectra were determined on each of the ten compounds and complete spectra are included in the Catalogs of Spectral Data.[8] Complete discussion of the spectra is beyond the scope of this paper. A few observations, with emphasis on the effect of the sulfur atom, can be made.

Mass Spectra.—The spectra of nine of the compounds were obtained with a Consolidated mass spectrometer, model 21-103 (21-102 modified). The electron current to the collector was automatically maintained at 10.5 microamperes and the temperature of the ion source at 250°. The spectrum of 2-propanethiol was obtained using the procedure described in a previous paper.[2]

---

(8) American Petroleum Institute Research Project 44. Carnegie Institute of Technology. Catalog of Mass Spectral Data. Catalog of Ultraviolet Spectral Data. Catalog of Infrared Spectral Data.

TABLE II

PROPERTIES OF TEN ORGANIC SULFUR COMPOUNDS

Cpd. no.	Compound	Impurity, mole %	F.p. for zero impurity, °C.	Cryoscopic constant A, deg.$^{-1}$	B.p. at 760 mm., °C.	Temp. of measurement, t, °C.	Density at t°C., g./ml.	Viscosity at t°C., centipoises	Surface tension at t°C., dynes per cm.
1	2-Propanethiol (isopropyl mercaptan)	0.02 ± 0.02	−130.54	0.033	52.6	20	0.81431	0.369	22.0
						25	.80864	.352	21.6
						30	.80312	.333	20.8
2	1-Butanethiol (*n*-butyl mercaptan)	0.04 ± .04	−115.67	.042	98.4	20	.84161	.497	26.1
						25	.83676	.471	25.6
						30	.83197	.445	25.1
3	2-Butanethiol (*sec*-butyl mercaptan)	0.1 ± .1	−140.14[a,b]	.044[b]	85.0	20	.82988	.463	24.4
						25	.82480	.438	23.7
						30	.81976	.415	23.1
4	2-Thiapropane (dimethyl sulfide)	0.01 ± .01	− 98.27	.027	37.4	20	.84825	.285	24.4
						25	.84230	.275	23.9
						30	.83634	.262	23.1
5	2-Thiapentane (methyl *n*-propyl sulfide)	0.03 ± .03	−112.97	.044	95.6	20	.84236	.468	25.9
						25	.83741	.444	25.3
						30	.83245	.420	24.7
6	3-Methyl-2-thiabutane (methyl isopropyl sulfide)	0.01 ± .01	−101.51	.036	84.8	20	.82990	.455	24.2
						25	.82486	.430	23.6
						30	.81978	.407	23.1
7	Thiacyclohexane (pentamethylene sulfide)	0.06 ± .06	+ 18.99	.004	141.8	20	.98557	2.440	35.1
						25	.98093	2.196	34.6
						30	.97633	1.985	33.9
8	2-Methylthiophene	0.04 ± .04	− 63.38	.025	112.5	20	1.01965	0.703	31.7
						25	1.01422	.660	31.1
						30	1.00891	.620	30.4
9	3-Methylthiophene	0.03 ± .03	− 68.94	.031	115.4	20	1.02183	.674	31.8
						25	1.01647	.635	31.0
						30	1.01136	.597	30.4
10	Benzo[b]thiophene (thianaphthene)	0.03 ± .01[b]	+ 31.34	.0153[b]	219.9	35	1.1988	2.517	42.6
						40	1.1937	2.423	41.8

[a] Triple point. [b] Determined by Thermodynamics Laboratory, Bureau of Mines, Bartlesville, Okla.

TABLE III

DERIVED FUNCTIONS

Compound	Refractivity intercept $n^{20}{}_D - \frac{d^{20}{}_4}{2}$	Specific dispersion $\frac{(n^{20}{}_F - n^{20}{}_C)10^4}{d^{20}{}_4}$	Mol. refraction $M/d\frac{n^2{}_D - 1}{n^2{}_D + 2}$	Mol. vol. $M/d^{20}{}_4$	Parachor $M\gamma^{1/4}/(D - d)$
2-Propanethiol	1.01838	119.2	23.941	93.527	202.8
1-Butanethiol	1.02217	114.1	28.408	107.159	242.2
2-Butanethiol	1.02179	113.9	28.446	108.673	241.7
2-Thiapropane	1.01134	122.3	19.132	73.250	163.1
2-Thiapentane	1.02317	115.3	28.446	107.063	241.6
3-Methyl-2-thiabutane	1.02419	117.7	28.592	108.671	241.1
Thiacyclohexane	1.01405	114.2	30.850	103.692	252.4
2-Methylthiophene	1.01052	161.6	29.284	96.272	228.5
3-Methylthiophene	1.00950	159.0	29.225	96.067	228.2
Benzo[b]thiophene	1.0351	...	39.93	110.53	286.0

Abridged mass spectra of the compounds are presented in Table IV. As with the previously reported compounds, many prominent rearrangement peaks are evident. The ion at m/e 35 (SH_3^+) is a particularly conspicuous rearrangement peak in the spectra of the thiols and sulfides. The sulfides show rearrangement peaks at m/e 48 and m/e 49. The probable configuration for these two ions is CH_3SH^+ and $CH_3SH_2^+$. 2-Thiapropane exhibits interesting rearrangement peaks in the C_2 mass range. The peak at m/e 27 ($C_2H_3^+$) is unexpected as it involves formation of a new carbon–carbon bond. The magnitude of the m/e 27 peak is comparable with that of many of the peaks resulting from simple splitting of the molecule.

The spectrum of thiacyclohexane contains numerous large rearrangement peaks. The peak at m/e 29 ($C_2H_5^+$) and that at m/e 43 ($C_3H_7^+$) are probably formed in a manner similar to like peaks in the spectra of hydrocarbons where the normal molecular formula shows no ethyl or propyl groups. The ion at m/e 67 probably results from the loss of SH_3 from the thiacyclohexane molecule. The base peak for thiacyclohexane occurs at m/e 87. This

TABLE IV

MASS SPECTRA

Mass no., *m/e*	Relative intensity									
	2-Propanethiol M.W. = 76	1-Butanethiol M.W. = 90	2-Butanethiol M.W. = 90	2-Thiapropane M.W. = 62	2-Thiapentane M.W. = 90	3-Methyl-2-thiabutane M.W. = 90	Thiacyclohexane M.W. = 102	2-Methylthiophene M.W. = 98	3-Methylthiophene M.W. = 98	Benzo[b]thiophene M.W. = 134
134										100.0
108										4.18
102							97.2			1.61
98							2.28	56.5	53.2	0.46
97							4.63	100.0	100.0	0.19
90		53.5	60.8		46.1	84.5	0.25	0.03	0.08	8.54
89		0.25	0.33		0.54	1.46	4.60			10.5
87		.07	.03		.02		100.0			0.91
76	63.3	.59	.70		.65	4.37	1.56	0.21	0.19	0.79
75	1.49	.24	4.39		9.57	95.1	1.55		.07	2.28
74	0.13	.07	0.54		0.57	0.86	22.7		.03	2.91
71	.53	.62	1.21		1.01	1.20	5.26	4.12	4.63	0.90
69	.85	.62	0.96		0.75	.79	20.1	6.67	6.59	7.88
68	.27	.07	0.19		0.12	.14	71.9	0.66	0.86	0.58
67							44.0		.01	7.88
62	1.23	1.40	3.18	80.5	4.92	0.43	4.83	2.18	.97	4.10
61	39.4	20.6	82.8	30.2	100.0	7.11	66.4	1.80	.90	2.40
60	2.69	2.73	13.1	0.45	0.88	3.00	47.3	0.76	.48	0.49
59	8.41	4.33	11.2	2.87	3.38	14.5	26.6	5.27	1.31	0.33
58	6.10	4.88	10.3	3.27	2.76	6.53	13.6	6.78	4.59	2.64
57	2.86	17.7	90.1	2.73	0.97	1.99	5.00	4.23	3.24	1.89
56	0.40	100.0	14.9	0.64	.15	0.24	14.4	0.33	0.37	0.49
55	0.05	12.3	11.9		.23	0.79	39.5	0.05	0.03	.35
49	1.05	3.25	1.73	4.26	18.7	41.9	2.65	3.04	3.34	.96
48	0.23	6.90	0.57	3.89	39.6	77.6	4.80	0.77	0.89	.15
47	5.47	41.4	15.6	100.0	23.0	50.2	36.1	2.30	2.25	.38
46	1.50	10.4	2.31	41.9	11.7	12.9	67.3	1.55	1.79	.22
45	10.4	17.4	15.5	61.5	24.6	34.8	73.3	22.4	25.5	8.18
43	100.0	12.3	0.52		19.2	83.3	1.68	0.03	0.09	0.55
41	67.9	87.2	100.0		34.4	100.0	69.9	0.41	0.35	0.44
39	29.9	21.4	29.7		18.0	42.1	65.2	14.2	10.3	6.59
35	16.3	9.53	14.3	35.0	14.2	1.75	5.06	0.05	0.05	
34	3.08	3.37	3.18	1.75	0.60	0.69	2.72	.24	.19	0.11
33	5.78	4.09	5.86	1.63	.57	1.06	2.85	.49	.40	.27
32	2.60	1.63	2.09	2.78	.79	1.37	4.48	1.74	1.23	.88
29	0.71	36.8	81.3	0.80	2.90	2.55	19.2	0.16	0.05	.71
27	62.5	56.2	55.4	20.6	34.4	54.3	69.3	8.03	8.15	1.71

is equivalent to the loss of a methyl group from the original molecule and could be considered a rearrangement peak, although the peak may also result from the loss of a methylene group and a hydrogen atom. In the same way as the base peak, the ion at *m/e* 55 could be considered a rearrangement peak, as it is equivalent to the loss of CH_3S from the molecule. Other rearrangement peaks are *m/e* 47 (CH_2SH^+ or CH_3S^+), *m/e* 35 (SH_3^+), and *m/e* 69. The *m/e* 69 peak probably results from the loss of SH or S plus H from the molecule.

The aromatic nucleus in the thiophenes is quite stable to electron bombardment, as shown by the absence of large ring-fragment peaks. For example, in the spectrum of benzo[b]thiophene, the largest of these is only 10.5% of the parent. The principal fragment peaks for benzo[b]thiophene result from breaking the five-membered ring to lose SCH forming the complementary peaks at *m/e* 89 and *m/e* 45. The peak at *m/e* 67 probably is due, in large part, to double ionization of the parent molecule.

The base peaks for 2-methylthiophene and 3-methylthiophene occur at *m/e* 97. From previous correlations of the mass spectra of thiophenes with molecular structure,[9] these peaks probably represent the loss of a hydrogen atom from the methyl group.

Ultraviolet Spectra.—The ultraviolet spectra were determined with a Cary ultraviolet spectrophotometer, model 11. To obtain the spectra of the sulfides, purified 2,2,4-trimethylpentane was used as a solvent. Purified cyclohexane was used as a solvent to obtain the spectra of the other compounds. The spectrum of each compound was scanned between 200 and 400 mμ.

A summary of the ultraviolet absorption data is given in Table V, which contains the maxima and minima in the spectrum of each compound. The molar extinction associated with each maximum or minimum also is given.

The spectra of the thiols and sulfides showed only broad bands similar to those reported previously.[2] In addition to the bands shown in the table, weak shoulders (molar extinctions less than 100) appeared in the spectra of the sulfides. These

---

(9) I. W. Kinney, Jr., and G. L. Cook, *Anal. Chem.*, **24**, 1391 (1952).

TABLE V

ULTRAVIOLET ABSORPTION DATA

Compound	$\lambda_{\text{max.}}$,[a] or $\lambda_{\text{min.}}$	ϵ, l./mole cm.
2-Propanethiol	225–230 (max.)	160
1-Butanethiol	225–230 (max.)	160
2-Butanethiol	225–230 (max.)	135
2-Thiapropane	210–215 (max.)	1000
2-Thiapentane	210–215 (max.)	1000
3-Methyl-2-thiabutane	210–215 (max.)	1000
Thiacyclohexane	210–215 (max.)	1000
2-Methylthiophene	234–235 (max.)	7820
3-Methylthiophene	234–235 (max.)	5600
Benzo[b]thiophene	228 (max.)	34000
	236 (shoulder)	*ca.* 13100
	244 (min.)	4480
	258 (max.)	5950
	264 (shoulder)	*ca.* 5200
	277 (min.)	1430
	281 (max.)	1640
	285 (min.)	1530
	289 (max.)	2300
	290 (min.)	2180
	291 (max.)	2300
	295 (min.)	710
	297.5 (max.)	3680

[a] Wave length of absorption maximum or minimum in mμ.

shoulders, at 225–235 mμ, appear to be typical of sulfide spectra.[10]

The spectrum of each of the methylthiophenes showed only a single broad maximum in the 234–235 mμ region. The spectrum of benzo[b]thiophene, however, contained fine structure. The spectrum of the latter compound is qualitatively similar to that of typical aromatic and aza-aromatic hydrocarbon systems.[11]

Infrared Spectra.—The infrared spectra were determined with a Perkin–Elmer spectrometer, model 12C (12B modified). The sample of benzo[b]thiophene was liquefied by adding 1 drop of carbon disulfide to 1.0 g. of sample. The spectrum was then obtained on the liquefied sample. The instrument accessories used with this and each of the nine normally liquid samples were described in a previous paper.[2]

The three thiols exhibit the typical S–H stretching band at 3.9 μ. There are two absorption peaks in the 11–12.2 μ region. At least one of these can be ascribed to the C–S–H bending vibration.[4]

The C–S stretching vibration should appear in the 13.0–15.5 μ region. The thiols and sulfides have medium to strong absorption peaks in or near this region. The thiophenes also have intense peaks in the region but this absorption in the spectra of the methylthiophenes has been assigned to a symmetrical hydrogen bending mode.[12] In the spectrum of benzo[b]thiophene, one of the three strong peaks in this region probably arises from a vibration of the four hydrogens on the ortho-substituted benzene ring.

In thiophenes the vibration of the sulfur atom between the two carbons gives rise to an absorption band near 8.0 μ.[12] This band is strong in the spectra of both 2- and 3-methylthiophene. In the spectrum of benzo[b]thiophene, a band, similar in position and intensity to that found in the spectra of the methylthiophenes, probably arises from the same cause. The band at 21.0–22.0 μ is characteristic of the thiophene nucleus.[12] This band is very weak in the 3-methylthiophene spectrum. The bicyclic compound benzo[b]thiophene also shows the 21.0–22.0 μ band.

The bands due to vibrations of the C–C and C–H linkages appear in the expected positions. The bands near 3.4 μ are assigned to C–H stretching vibrations, those near 7.2 and 13.6 μ to vibrations of the methyl and methylene groups. The thiophenes have a band near 3.2 μ that is analogous to the C–H stretching vibrations of aromatic hydrocarbons. In the spectrum of benzo[b]thiophene, the 5.0-6.0 μ region is typical of the spectrum of an *ortho*-disubstituted benzene.[13] Additional vibrational assignments have been made for thiacyclohexane, 3-methylthiophene and 2-propanethiol.[4]

Acknowledgments.—This work was done under a coöperative agreement between the Bureau of Mines, United States Department of Interior, and the University of Wyoming. The authors wish to express their thanks to C. W. Bailey for obtaining the infrared and ultraviolet spectra.

---

(10) E. A. Fehnel and M. J. Carmack, *J. Am. Chem. Soc.*, **71**, 84 (1949).

(11) G. M. Badger and R. S. Pearce, *J. Chem. Soc.*, 3072 (1950); G. M. Badger, R. S. Pearce and R. Pettit, *ibid.*, 3199 (1951).

(12) H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 125.

(13) C. W. Young, R. B. Duvall and Norman Wright, *Anal. Chem.*, **23**, 709 (1951).