which is being held constant in the given series of experiments.

The results found for mechanism III are of special interest, since this mechanism has been postulated in order to explain the anomalous variation of Michaelis constant with substrate in the glucose oxidase–glucose–oxygen system.[6a] Although this mechanism accounts for the observed 7-fold variation in the Michaelis constant with 20-fold variation in oxygen pressure, it also predicts that $V_{\max_{A\ (\text{or } B)}}$ is linear with the substrate concentration B (or A), which is contrary to experimental facts. Experiments show[6a] that both $V_{\max_{\text{glucose}}}$ dependence on oxygen pressure and $V_{\max_{\text{oxygen}}}$ dependence on glucose concentration are not linear relationships but appear to obey the usual Michaelis–Menten law.

An explanation for, both, the variations of the Michaelis constant and of $V_{\max_{A\ (\text{or } B)}}$, can be offered in terms of mechanism I or II involving ternary complexes. Under the conditions, $V \rightarrow V_{\max_{A\ (\text{or } B)}}$, which prevailed during the experiments, the Michaelis constants would be expected to vary with concentrations of the reactants as shown in Table II and the maximum velocities, $V_{\max_{A\ (\text{or } B)}}$, would also vary as shown in Table I.

A similar explanation may be offered for the results of Tappel, Boyer and Lundberg,[6b] who found a 10-fold increase in the Michaelis constant for oxygen as the reducing substrate (linoleate) was increased 20-fold in a study of the reaction kinetics of soybean lipoxidase.

We see now that a variation in the Michaelis constant is to be expected if it is measured under conditions $V \rightarrow V_{\max_{A\ (\text{or } B)}}$ instead of the conditions $V_{\max_{A\ (\text{or } B)}} \rightarrow V_{\max_{AB}}$. Perhaps the term Michaelis constant should be reserved for the latter conditions, which yield a constant analogous to that derived for the classical one-reactant system.[5]

There are certainly many other mechanisms or variations of these mechanisms that could be discussed. We have pointed out one commonly postulated mechanism III that can usually be eliminated by the above analysis and have discussed two mechanisms (I and II) that demonstrate the pitfalls involved in measuring Michaelis constants.

It is important to note at this time that mechanisms I and II are special and simpler cases of a more general formulation which yields essentially the same kinetics. This formulation, previously mentioned by Laidler and Socquet,[13] is

$$\begin{aligned} E_1 + A &\rightleftharpoons E_2 + W \\ E_2 + B &\rightleftharpoons E_3 + X \\ E_3 &\longrightarrow P + E \end{aligned}$$

where E_2 and E_3 are modified forms of the enzyme, and W, X and P are products of the reactions. If W and X are non-existent, the above mechanism reduces to mechanism I or II and E_3 becomes a ternary enzyme–substrate complex. Thus, the concept of a ternary complex is not essential for the conclusions drawn concerning mechanisms I and II. However, the more general formulation above would require that the rate of the reaction would also be a function of the concentrations of the products W and X.

Acknowledgment.—We greatly appreciate the helpful discussions with Dr. Hans Lineweaver during the preparation of this paper.

PURIFICATION AND PROPERTIES OF TEN ORGANIC SULFUR COMPOUNDS[1]

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Ten organic sulfur compounds, ethanethiol, 2-methyl-2-propanethiol, 1-pentanethiol, 2-thiabutane, 3-thiapentane, thiacyclobutane, thiacyclopentane, 2,3-dithiabutane, 3,4-dithiahexane and thiophene, were purified to at least 99.9 mole % purity. The stability of the compounds under storage and distillation conditions was investigated. In addition to the boiling point and freezing point, 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 molar volume were calculated and are discussed briefly. Mass, infrared and ultraviolet spectra were determined permitting some correlation of the effect of sulfur groupings on spectra.

Literature surveys[2] have shown that data on the physical properties of thiols, sulfides, disulfides and thiophenes are meager. Many of the data available are unreliable because they were determined on compounds of doubtful purity. Because these types of compounds occur in petroleum products, the Bureau of Mines and the American Petroleum Institute have coöperatively sponsored Research Project 48. This Project has among its purposes the production of sulfur compounds in high purity and the accurate determination of their physical properties. The attainment and measurement of the high purities are facilitated by the purification of a large quantity of each compound from which samples are available for sale by the American Petroleum Institute as calibration standards. Because of this latter activity, the stability of the compounds has been investigated.

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(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.

(2) W. E. Haines, W. J. Wenger, R. V. Helm and J. S. Ball, *U. S. Bur. Mines, Rept. Invest.*, 4060 (1946); R. V. Helm, W. E. Haines and J. S. Ball, *ibid.*, 4566 (1949).

Three groups of physical properties are determined: (1) common physical properties such as refractive index, density, viscosity, surface tension, melting point and boiling point; (2) thermodynamic properties; and (3) spectroscopic patterns. This paper reports properties in the first and third groups for ten sulfur compounds. The thermodynamic properties are reported in separate papers.[3]

The first ten sulfur compounds selected for purification were representative of the four types expected in petroleum: Three thiols (ethanethiol, 2-methyl-2-propanethiol and 1-pentanethiol); four sulfides (2-thiabutane, 3-thiapentane, thiacyclobutane and thiacyclopentane); two disulfides (2,3-dithiabutane and 3,4-dithiahexane); and thiophene.

Purification

To meet the needs of the program, a minimum of 1.5 liters of material with a purity of at least 99.9 mole % was required. Whenever possible, the compounds for purification were obtained from commercial sources; however, it was necessary to synthesize two of the compounds. The purification procedure was similar to that used for hydrocarbons by the National Bureau of Standards.[4] After preliminary purification by chemical procedures, a distillation was made, taking 30-ml. fractions. From density or refractive index determinations, certain fractions were selected for determination of purity by the freezing point method.[5] High purity fractions were combined, and the composite was tested for impurity by determining freezing point and mass spectra before it was sealed "in vacuum."[6] Variations in the procedure were made for individual compounds as described below. All distillations were made at atmospheric pressure (585 mm.) unless otherwise noted.

Ethanethiol.—A distillation of 2.5 l. of Eastman Kodak Co. "blue label" ethanethiol yielded insufficient material (0.6 l.). Therefore, 3 l. of "white-label" ethanethiol was added and was passed through silica gel to remove the water. Distillation was through a column 1 inch in diameter, having a 9-foot section packed with stainless-steel helices (hereafter designated as column 1). Yield of high-purity (99.95 mole %) material was 1.95 l.

2-Methyl-2-propanethiol.—Approximately 7 l. of 2-methyl-2-propanethiol donated by Phillips Petroleum Co. was distilled through a 1-inch by 8-foot glass Oldershaw column having 80 perforated plates (column 2). Yield of high-purity (99.92 mole %) material was 2.1 l.

1-Pentanethiol.—This compound was prepared by treating *n*-pentyl bromide with sodium hydrosulfide in alcoholic solution according to the general procedure of Ellis and Reid.[7] Several batches were prepared, the largest of which was 7 moles. Yields were 85–90% of theoretical. Oil-soluble impurities were removed from the crude thiol by ether extraction of the water-soluble sodium mercaptide. The thiol was regenerated, dried and 2.6 l. was distilled through column 1. Yield of high-purity (99.92 mole %) material was 2.4 liters.

2-Thiabutane.—Approximately 3 l. of 2-thiabutane (Eastman Kodak Co.) was distilled through a high-temperature Podbielniak heligrid column with a 5-foot packed section (column 3). Yield of high-purity (99.96 mole %) material was 1.53 l.

3-Thiapentane.—Approximately 3 l. of 3-thiapentane (Eastman Kodak Co.) was distilled through column 1. This distillation was made before freezing-point equipment was available, so that fractions were chosen on the basis of refractive index. Purity was measured on the composite at a later date. Yield of high-purity (99.94 mole %) material was 1.68 l.

Thiacyclobutane.—The method of synthesis was supplied by Bordwell and Pitt.[8] A mixture of 304 g. (4 moles) of thiourea, 819 g. of 1-bromo-3-chloropropane and 1.5 l. of ethanol was refluxed for 5 hours. The solvent was removed from the reaction mixture by distillation at atmospheric pressure up to a flask temperature of 90°. Excess halide was removed by heating the flask at 60–70°, for 2 hours under vacuum (20 mm.). The thiouronium salt was dissolved in 350 ml. of water and was added over a period of 2 hours to a solution of 513 g. of potassium hydroxide in 1.2 l. of water. The mixture was held at 60–80° during the addition and for 1 hour afterward. The reaction mixture was cooled by adding ice and the sulfide layer separated. The water layer was extracted with ether. Thirty-seven separate 4-mole batches were made, with an average yield of 53.5%.

The crude thiacyclobutane (5.8 l.) thus prepared was dried over anhydrous potassium carbonate and charged to column 3 for distillation. The composite was dried by low-temperature filtration and over anhydrous calcium sulfate before it was sealed "in vacuum." Yield of high-purity (99.95 mole %) material was 2.0 l.

Thiacyclopentane.—Nearly 10 l. of thiacyclopentane contributed by Oronite Chemical Co. was distilled through column 3. The high-purity composite was dried by a low-temperature filtration and then over anhydrous calcium sulfate and silica gel just before it was sealed "in vacuum." Yield of high-purity (99.95 mole %) material was 1.86 liters.

2,3-Dithiabutane.—Nearly 3 l. of 2,3-dithiabutane (Eastman Kodak Co.) was distilled through a column 1 inch in diameter having a 6-foot section packed with Stedman packing (column 4). Yield of high-purity (99.97 mole %) material was 1.6 l.

3,4-Dithiahexane.—Five liters of 3,4-dithiahexane (Eastman Kodak Co.) was distilled through column 4 at a pressure of 50 mm. Two separate distillations were made, and the high-purity fractions were combined. The yield of high-purity (99.90 mole %) material was 2.15 l.

Thiophene.—Nearly 4.5 l. of thiophene (Socony—Vacuum Oil Co.) was distilled through column 1. The high-purity (99.99 mole %) material (1.9 l.) was shown to be benzene free by means of the mass spectrometer. A benzene impurity would not be shown by the freezing-point method, because benzene and thiophene form a solid solution.[9]

Stability

Inasmuch as a portion of each of these compounds has been set aside as a standard sample, the storage stability was tested in the following manner. Samples of the purified compounds were sealed "in vacuum" in clear glass ampoules and exposed to sunlight for 1 year. Control samples were kept in the dark during the same period. Determinations of purity by the freezing-point method were then made on both the exposed and the control samples. The greatest variation in purity shown by the dark storage samples was 0.03 mole %, which is within experimental error.

Six of the compounds showed no decrease in purity after 1 year in strong sunlight. Of those affected by sunlight, two were easily separated from the impurity by a simple room-temperature vacuum transfer. Thiacyclobutane forms polymer upon exposure to light. Polymerization was evident after 2 weeks' exposure, and at the end of a year this sample was a thick white slurry. However, when the unpolymerized liquid was vacuum-transferred from the ampoule and analyzed by the mass spectrometer (there was insufficient volume for freezing-point determination) the pattern obtained was identical to that of the original sample. Polymerization may occur in 2-methyl-2-propanethiol to a very minor extent, as evidenced by a reduction in purity too small to be conclusive. Vacuum transfer again yielded material of the original purity.

Only the two disulfides showed significant deterioration, because some of the impurities formed are volatile so that they cannot be separated by a vacuum transfer. 2,3-Dithiabutane that had an original purity of 99.97 mole % was only 91.8 mole % after exposure to sunlight for a year.

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[3] G. Waddington, H. M. Huffman and co-workers, *J. Am. Chem. Soc.*, **71**, 797 (1949); **72**, 2424 (1950); **73**, 261 (1951); **74**, 2801, 2804, 2478, 4656, 6025 (1952); **75**, 2795, 1818 (1953).

[4] A. J. Streiff, E. T. Murphy, V. A. Sedlak, C. B. Willingham and F. D. Rossini, *J. Research Natl. Bur. Standards*, **37**, 331 (1946).

[5] A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, *ibid.*, **35**, 355 (1945).

[6] B. J. Mair, D. J. Termini, C. B. Willingham and F. D. Rossini, *ibid.*, **37**, 229 (1946).

[7] L. M. Ellis, Jr., and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 1674 (1932).

[8] F. G. Bordwell and B. M. Pitt, private communication from API Project 48B at Northwestern University.

[9] F. S. Fawcett and H. E. Rasmussen, *J. Am. Chem. Soc.*, **67**, 1705 (1945).

TABLE I

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°, g./ml.	Viscosity at t° C., centipoises	Surface tension at t° C., dynes per cm.
1	Ethanethiol	0.05 ± 0.04	−147.89	0.036	35.0				
	(ethyl mercaptan)					20	0.83914	0.293	23.5
						25	.83316	.279	22.8
						30	[a]	[a]	[a]
2	2-Methyl-2-propanethiol	.08 ± .04	+ 1.11	.005	64.2				
	(*t*-butyl mercaptan)					20	.80020	.638	20.8
						25	.79472	.588	20.2
						30	.78929	.544	19.6
3	1-Pentanethiol	.08 ± .05	− 75.70	.048	126.5				
	(*n*-pentyl mercaptan)					20	.84209	.639	26.8
						25	.83763	.601	26.3
						30	.83317	.568	25.7
4	2-Thiabutane	.04 ± .04	−105.91	.04	66.7				
	(methyl ethyl sulfide)					20	.84221	.373	24.9
						25	.83679	.354	24.2
						30	.83145	.337	23.4
5	3-Thiapentane	.06 ± .04	−103.93	.04	92.1				
	(ethyl sulfide)					20	.83623	.440	25.2
						25	.83120	.417	24.5
						30	.82625	.396	23.9
6	Thiacyclobutane	.05 ± .05	− 73.25	.023	95.0				
	(trimethylene sulfide)					20	1.02000	.638	36.3
						25	1.01472	.607	35.6
						30	1.00957	.576	35.0
7	Thiacyclopentane	.05 ± .05	− 96.16	.028	120.9				
	(tetrahydrothiophene)					20	0.99869	1.042	35.8
						25	.99379	0.971	35.0
						30	.98928	.914	34.6
8	2,3-Dithiabutane	.03 ± .02	− 84.72	.030	109.6				
	(dimethyl disulfide)					20	1.06250	.619	33.6
						25	1.05690	.585	32.8
						30	1.05138	.555	32.2
9	3,4-Dithiahexane	.10 ± .08	−101.52	.038	152.6				
	(diethyl disulfide)					20	0.99311	.860	31.3
						25	.98818	.805	30.7
						30	.98332	.757	30.2
10	Thiophene	.013 ± .011	− 38.24	.0114	84.1				
						20	1.06485	.654	32.8
						25	1.05887	.613	32.0
						30	1.05309	.576	31.1

[a] This compound has a boiling point of 27.8° at 585 mm.

Vacuum transfer improved the purity to 96.3 mole %. 3,4-Dithiahexane deteriorated from 99.92 to 96.3 mole %. After vacuum transfer the purity was 98.1 mole %. Thus these two samples should be stored in the dark in order to maintain high purity.

A test of stability under distillation conditions was made by refluxing each of the pure sulfur compounds in an all-glass system at atmospheric pressure for 240 hours. The system was vented through a sodium hydroxide absorber and a Dry Ice trap to retain any decomposition products. After the reflux period, the sample was tested for purity, and the absorbers were examined for decomposition products.

The two disulfides were the only compounds that showed evidence of decomposition under these conditions. Both released traces of hydrogen sulfide and/or thiol and darkened. However, in contrast to the storage stability results, 3,4-dithiahexane showed the greater decomposition, its purity being reduced 0.6 mole % while the 2,3-dithiabutane showed a reduction of less than 0.1 mole %. This may be due to the higher reflux temperature of the 3,4-dithiahexane.

Physical Properties

Physical property data for the ten organic sulfur compounds are shown in Tables I and II. No comparison with literature values has been made in this paper, but excellent agreement may be noted for those values reported in recent papers on thiophene,[9] 2-thiabutane, 3-thiapentane, 2,3-dithiabutane, 3,4-dithiahexane[10] and thiacyclopentane.[11] Descriptions of apparatus, procedures and estimates of accuracy are included in the experimental section.

Experimental

Freezing Point, Purity and Cryoscopic Constants.—The freezing points were determined and the purities calculated from the time–temperature freezing and melting curves, according to the method of Glasgow, Streiff and Rossini.[5] Three different "impurities" were used in determining the cryoscopic constant, A. Accuracy of freezing points is estimated to be ±0.01°.

Boiling Point.—The boiling points were measured in a Cottrell ebulliometer, using a platinum resistance thermohm. The pressure was maintained by a Cartesian manostat (Emil Greiner), using an atmosphere of dry nitrogen. The pres-

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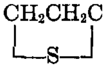
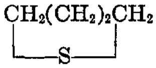
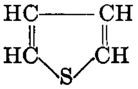
[10] D. T. McAllan, T. V. Cullum, R. A. Dean and F. A. Fidler, *J. Am. Chem. Soc.*, **73**, 3627 (1951).

[11] E. V. Whitehead, R. A. Dean and F. A. Fidler, *ibid.*, **73**, 3632 (1951).

TABLE II

REFRACTIVE INDICES OF TEN ORGANIC SULFUR COMPOUNDS

Cpd. no.	Compound	Temp. of measurement, t, °C.	Refractive indices						
			Helium r line n^t	Hydrogen C line n^t	Sodium D line n^t	Mercury e line n^t	Helium v line n^t	Hydrogen F line n^t	Mercury g line n^t
1	C_2H_5SH	20	1.42763	1.42810	1.43105	1.43356	1.43695	1.43836	1.44428
		25	1.42442	1.42486	1.42779	1.43027	1.43363	1.43505	1.44085
		30	[a]	[a]	[a]	[a]	[a]	[a]	[a]
2	*t*-C_4H_9SH	20	1.41992	1.42046	1.42320	1.42550	1.42852	1.42991	1.43534
		25	1.41699	1.41739	1.42007	1.42230	1.42545	1.42677	1.43214
		30	1.41392	1.41431	1.41697	1.41930	1.42231	1.42362	1.42894
3	$C_5H_{11}SH$	20	1.44374	1.44420	1.44692	1.44922	1.45224	1.45360	1.45902
		25	1.44121	1.44170	1.44439	1.44666	1.44974	1.45104	1.45639
		30	1.43872	1.43912	1.44180	1.44410	1.44707	1.44841	1.45371
4	$CH_3SC_2H_5$	20	1.43703	1.43747	1.44035	1.44278	1.44616	1.44759	1.45334
		25	1.43410	1.43450	1.43737	1.43984	1.44302	1.44455	1.45028
		30	1.43115	1.43153	1.43437	1.43678	1.44005	1.44146	1.44715
5	$(C_2H_5)_2S$	20	1.43971	1.44015	1.44298	1.44539	1.44858	1.44998	1.45568
		25	1.43695	1.43736	1.44017	1.44256	1.44577	1.44716	1.45280
		30	1.43408	1.43453	1.43734	1.43972	1.44290	1.44428	1.44988
6		20	1.50603	1.50660	1.51020	1.51330	1.51737	1.51922	1.52648
		25	1.50318	1.50379	1.50738	1.51050	1.51453	1.51635	1.52362
		30	1.50035	1.50093	1.50448	1.50755	1.51154	1.51337	1.52059
7		20	1.50101	1.50154	1.50483	1.50764	1.51132	1.51295	1.51945
		25	1.49840	1.49891	1.50217	1.50495	1.50864	1.51021	1.51676
		30	1.49583	1.49634	1.49962	1.50237	1.50600	1.50761	1.51408
8	CH_3SSCH_3	20	1.52103	1.52163	1.52592	1.52970	1.53473	1.53683	1.54577
		25	1.51803	1.51871	1.52298	1.52669	1.53174	1.53387	1.54270
		30	1.51512	1.51575	1.51998	1.52366	1.52860	1.53075	1.53958
9	$C_2H_5SSC_2H_5$	20	1.50299	1.50354	1.50731	1.51055	1.51491	1.51680	1.52453
		25	1.50035	1.50097	1.50470	1.50793	1.51230	1.51411	1.52179
		30	1.49771	1.49826	1.50198	1.50524	1.50947	1.51140	1.51899
10		20	1.52339	1.52403	1.52890	1.53317	1.53888	1.54135	1.55174
		25	1.52019	1.52087	1.52572	1.52991	1.53566	1.53814	1.54838
		30	1.51708	1.51778	1.52257	1.52674	1.53245	1.53484	1.54507

[a] This compound has a boiling point of 27.8° at 585 mm.

sure was measured with a barometer, which had been calibrated using the vapor pressure of water as a standard. The accuracy of the boiling point data is estimated to be 0.1°.

Refractive Index.—Refractive indices were measured with a Bausch and Lomb Precision Oil Refractometer, Abbe type, enclosed in a specially built housing to eliminate convection currents. Data were obtained at 20, 25 and 30° for seven different wave lengths of light. The temperatures were maintained by circulating water, thermostated to a maximum variation of ± 0.005° as measured by a platinum resistance thermohm positioned in the refractometer. The room temperature was maintained within 1° of the temperature of measurement. The refractometer was calibrated with samples of toluene, 2,2,4-trimethylpentane and methylcyclohexane, which had been certified with respect to refractive index by the National Bureau of Standards. Duplicate determinations indicate a precision of ±0.00003. Accuracy of reported values is estimated at ±0.00006.

TABLE III

CORNING FILTERS USED FOR VARIOUS WAVE LENGTHS

Line		Wave length, Å.	Color	Corning filter no.
Helium	r	6678.1	Red	2424
Hydrogen	C	6562.8	Red	None required
Sodium	D	5892.6[a]	Yellow	None required
Mercury	e	5460.7	Green	3484, 5120, 4303
Helium	v	5015.7	Green	5031, 3387, 5120
Hydrogen	F	4861.3	Green	5031, 3387
Mercury	g	4358.3	Blue	3389, 5113

[a] Intensity weighted mean of the doublet, D_1, D_2.

The seven wave lengths of light were obtained from four different light sources: The standard "Sodium Lab Arc" furnished with the refractometer, the H-4 type capillary mercury arc available as an accessory to the instrument, a hydrogen-discharge lamp manufactured by Rankin Glass Blowing Co., and a helium spectrum tube with a narrow capillary for brilliant discharge. The Corning filters shown in Table III were used to isolate the specific wave lengths. These filters were checked for transmittancy over the visible range by means of a spectrophotometer and found satisfactory.

Density.—Densities were determined at 20, 25 and 30° with a Christian Becker chainomatic 5-place specific gravity balance with a 5-gram displacement plummet. The sample was placed in a vacuum-jacketed bath through which water, thermostated to ±0.005°, was passed during the determination. The balance was calibrated with a set of standard weights and with toluene, methylcyclohexane and 2,2,4-trimethylpentane as described by Forziati, *et al.*[12] Duplicate determinations show a precision of ±0.00003. The accuracy is estimated to be ±0.00005 g./ml.

Viscosity.—Viscosities were determined using two Geist–Cannon viscometers designed for non-viscous fluids.[13] A 4.0-ml. charge was pipetted at the temperature of measurement and the viscometer was made vertical in a bath thermostated to ±0.005°. At least two consecutive efflux times, agreeing within 0.1 second, were obtained. The viscometers were calibrated with conductance water and had efflux times of 315.0 and 415.4 seconds at 20°. Corrections were

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[12] A. F. Forziati, B. J. Mair and F. D. Rossini, *J. Research Natl. Bur. Standards*, **35**, 513 (1945).

[13] J. M. Geist and M. R. Cannon, *Ind. Eng. Chem., Anal. Ed.*, **18**, 611 (1946).

TABLE IV

DERIVED FUNCTIONS

Compound	Refractivity intercept $n^{20}_D - d^{20}_4$	Specific dispersion $\frac{(n^{20}_F - n^{20}_C)10^4}{d^{20}_4}$	Molecular refraction $M/d \frac{(n_D^2 - 1)}{(n_D^2 + 2)}$ Obsd.	Calcd.	Parachor $M\gamma^{1/4}/(D - d)$ Obsd.	Calcd. Sugden	M. & P.	Molar volume $M/d_{b.p.}$ Obsd.	Calcd. Kopp	LeBas
Ethanethiol	1.01148	122.27	19.13	19.24	163.0	160.4	160.8	75.5	77.6	74.4
2-Methyl-2-propanethiol	1.02310	118.09	28.65	28.47	240.5	238.4	240.8	119.7	121.6	118.8
1-Pentanethiol	1.02588	111.63	32.99	33.09	281.0	277.4	280.8	139.2	143.6	141.0
2-Thiabutane	1.01925	120.16	23.80	24.05	201.7	199.4	200.8	96.0	99.6	96.6
3-Thiapentane	1.02487	117.55	28.53	28.67	241.3	238.4	240.8	117.8	121.6	118.8
Thiacyclobutane	1.00020	123.72	21.71	21.85	178.1	176.8	176.0	78.6	88.6	89.2
Thiacyclopentane	1.00549	114.25	26.13	26.47	215.6	212.7	213.0	97.4	110.6	111.4
2,3-Dithiabutane	0.99467	143.06	27.15	27.44	213.0	208.6	210.8	97.6	100.2	97.0
3,4-Dithiahexane	1.01076	133.52	36.58	36.67	290.6	286.6	290.8	141.3	144.2	141.4
Thiophene	0.99648	162.65	24.32	24.80	188.8	190.7	189.4	84.9	88.6	96.6

made for kinetic energy losses. A calibration value of 1.002 centipoise for water at 20° was used.[14] This value has recently been adopted by the National Bureau of Standards for use in certifying the viscosity of standard oils. The precision of the measurements was ±0.03%, and the accuracy is estimated to be ±0.001 centipoise.

Surface Tension.—Surface tensions were measured in Pyrex capillarimeters of U-tube design similar to those described in the literature.[15] One arm was constructed of precision-bore capillary tubing 0.05 cm. in diameter. The other arm was of large enough bore (4 cm.) to give a flat meniscus.[16] Surface tension was measured by adjusting the liquid level to a fine calibration mark on the capillary tube; the instrument was made vertical in a bath thermostated to ±0.005° and the capillary rise was measured by means of a cathetometer. Duplicate determinations were made for each compound, using two capillarimeters and making corrections as described in the literature.[17] Pure benzene, which was assumed to have a surface tension of 28.88 dynes/cm. at 20°,[18] was used for calibration. Precision of the method is ±0.05 dyne/cm. with an estimated accuracy of ±0.1 dyne/cm.

Derived Functions.—Two types of derived functions were calculated using the determined constants. Specific dispersion and refractivity intercept, used analytically to distinguish different classes of hydrocarbons, are functions of the non-additive type. The additive functions are molecular refraction, parachor and molar volume. All functions shown in Table IV were calculated at 20° except molar volume.

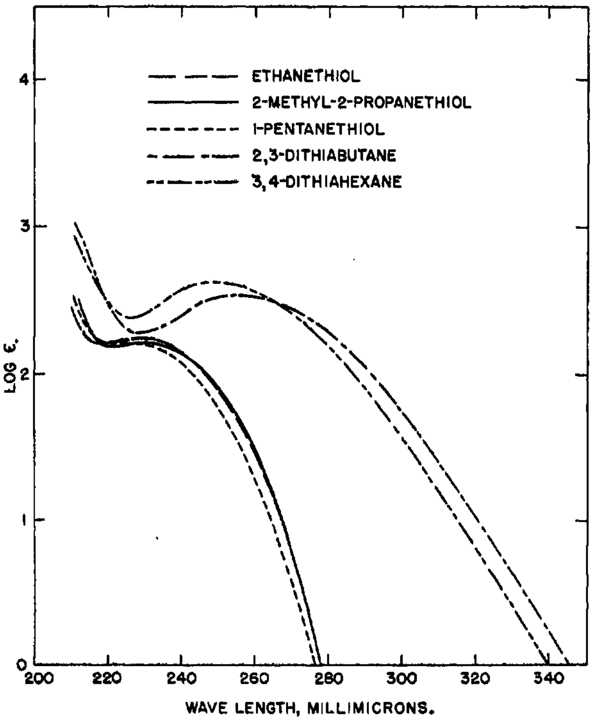

Fig. 1.—Ultraviolet spectra of thiols and disulfides.

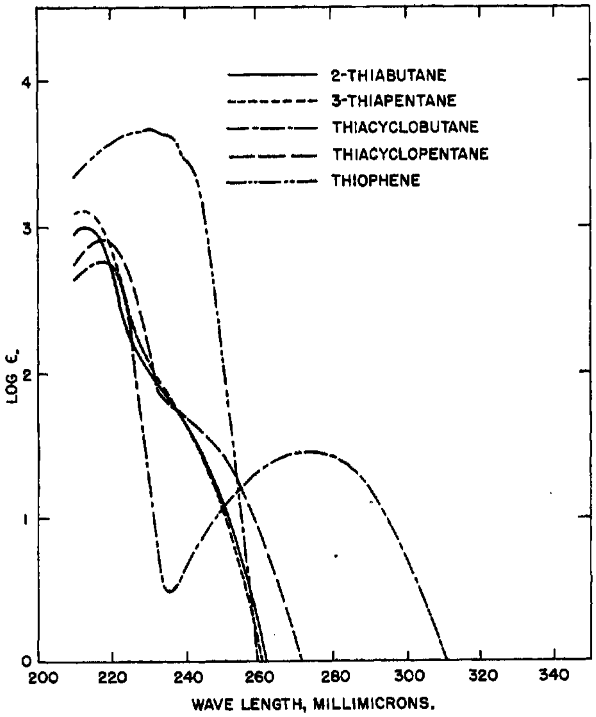

Fig. 2.—Ultraviolet spectra of sulfides and thiophene.

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[14] J. F. Swindells, J. R. Coe, Jr., and T. B. Godfrey, *J. Research Natl. Bur. Standards*, **48**, 1 (1952).

[15] G. Jones and W. A. Ray, *J. Am. Chem. Soc.*, **59**, 187 (1937).

[16] T. W. Richards and L. B. Coombs, *ibid.*, **37**, 1657 (1915).

[17] A. Weissberger, "Technique of Organic Chemistry, Volume I, Physical Methods of Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, p. 366.

[18] "International Critical Tables," Vol. IV, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 454.

TABLE V

MASS SPECTRA

Mass no., m/e	Relative intensity									
	Ethanethiol M.W. = 62	2-Methyl-2-propanethiol M.W. = 90	1-Pentanethiol M.W. = 104	2-Thiabutane M.W. = 76	3-Thiapentane M.W. = 90	Thiacyclobutane M.W. = 74	Thiacyclopentane M.W. = 88	2,3-Dithiabutane M.W. = 94	3,4-Dithiahexane M.W. = 122	Thiophene M.W. = 84
122									76.5	
104			32.4							
94								100.0	53.0	
90		43.8			70.4		2.33		0.10	
88		0.01	0.01				52.0			0.02
84		0.01					0.16			100.0
79								59.4	8.99	
76		0.84	0.40	64.0	3.85	1.86	0.03	0.47	0.15	
75		20.0	0.53	3.81	100.0	1.71	0.18		0.37	
74		0.70	0.48	0.09	0.02	42.0	0.16			
70		0.10	36.7		0.05	0.17	0.09		0.31	0.34
66			0.12					0.97	90.3	
65	0.11		0.22					0.46	4.00	
64	4.24		0.09	0.11	2.20		0.01	11.2	9.92	
62	96.5	0.06	1.50	3.09	50.8		4.46	0.68	3.73	
61	15.3	0.93	13.7	100.0	58.1	0.09	4.10	12.2	8.36	0.10
60	1.38	0.45	2.33	2.86	11.6	0.17	100.0	0.25	12.1	2.83
58	10.3	6.82	2.13	4.73	9.36	1.89	8.00	0.21	6.99	64.8
57	8.03	84.4	3.79	2.37	4.36	0.96	2.52	0.13	2.91	12.9
55		5.91	46.7		0.48		12.3		0.12	
48	2.13	0.39	4.07	56.0	2.69	4.57	2.18	14.3	0.37	0.67
47	80.4	10.4	27.8	43.3	93.4	7.23	28.1	26.4	4.89	2.55
46	15.2	1.07	5.66	13.7	17.7	100.0	33.1	37.6	5.72	1.41
45	24.4	6.43	10.6	27.9	23.2	24.6	38.1	62.6	17.7	57.8
42		4.21	100.0	0.44	0.24	0.42	4.21		0.07	4.43
41		100.0	41.1	4.83	6.38	8.35	10.4		0.42	2.10
39		30.5	18.7	0.75	0.75	9.59	13.3		0.24	28.6
35	15.3	0.91	4.31	21.9	19.4	0.79	0.94	0.92	9.92	
34	25.9	2.10	1.87	0.87	6.87	0.40	1.52	0.43	2.68	0.39
33	9.50	4.74	1.71	1.15	1.78	0.81	1.28	1.28	2.08	0.87
32	5.80	1.85	0.82	1.26	1.12	1.85	1.56	3.58	2.21	3.65
29	100.0	65.1	33.9	21.6	56.3	0.64	3.24	0.14	100.0	0.12
27	81.2	22.0	34.3	41.1	73.3	8.08	23.6	0.92	70.2	1.64

Refractivity-intercept values of all the compounds are low compared with corresponding values for hydrocarbons. The cyclic sulfur compounds and the disulfides show lower values than the rest of the compounds. On the basis of specific dispersion, the compounds are divided into three groups: the thiols and sulfides have values in the range 110–125; the disulfides, in the range 130–145; and thiophene, 162.6. These values correspond to those for olefins, diolefins and aromatics in the hydrocarbon series, as might be expected from the equivalence of the sulfur atom and the ethylenic group.[19]

The observed molecular refractions agree with the calculated values within 2%; but all are low, except for 2-methyl-2-propanethiol, the only compound studied with a tertiary linkage. Calculations are based on the increments of Eisenlohr[20] for carbon and hydrogen and Boudet and Rambaud[21] for sulfur. The latter workers suggest different increments for sulfur in different types of linkages. A value of 7.81 has been assigned to sulfur in aliphatic thiols; 8.00, in alkyl sulfides; and 7.26, in substituted thiophenes. If sulfur increments are calculated from the reported data, assuming the carbon and hydrogen increments to be correct, values of 7.8 ± 0.2 for sulfur in aliphatic thiols, 7.7 ± 0.1 in sulfides, 7.9 ± 0.1 in disulfides, and 6.8 in thiophene are obtained. Thus, except for thiophene, the values differ so much within the various types that assignment of different increments seems unwarranted.

Parachor values were calculated using increments from the work of Sugden[22] and also from Mumford and Phillips.[23] Although the agreement with the observed values is good using the increments of the latter workers, both calculations yield parachors that are lower than the observed, except for thiophene and 2-methyl-2-propanethiol. Mumford and Phillips use higher values for both CH_2 (40.0) and sulfur (50.0) than Sugden (39.0 and 48.2, respectively). Slightly higher values would bring the results into better agreement. Observed molar volumes were based on densities at the boiling point obtained by straight-line extrapolation of the reported data. Calculated values were obtained by using the increments of Kopp[24] and also by using the carbon and hydrogen increments

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(19) F. C. Whitmore, "Organic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1937, p. 884.

(20) A. Weissberger, ref. 17, p. 1163.

(21) R. Boudet and R. Rambaud, *Bull. soc. chim. France*, 793 (1948): *C. A.*, **43**, 13 (1949).

(22) A. Weissberger, ref. 17, p. 418.

(23) *Ibid.*, p. 416.

(24) S. Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 525.

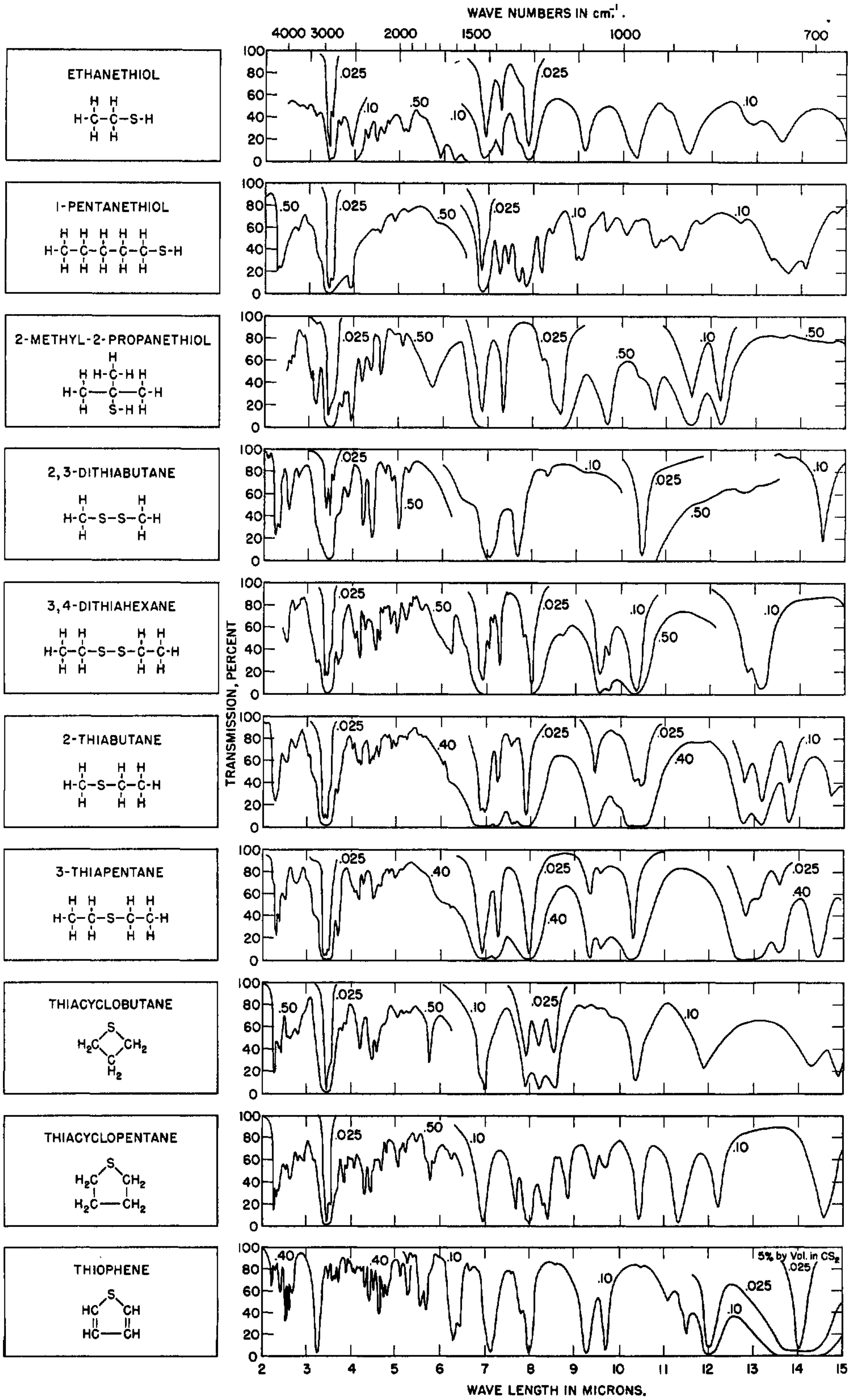

Fig. 3.—Infrared spectra (2–15 μ) of ten sulfur compounds.

of LeBas[24] together with the sulfur increment of Kopp. (LeBas does not report an increment for sulfur.) Values obtained from the latter calculation fit the data much better than those based on the Kopp increments. The three cyclic compounds show extreme deviations because no allowance has been made for the decrease in molar volume caused by cyclization.

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.[25] A thorough discussion of the spectra will have to await the determination of data on more members of the various homologous series, but some observations can be made especially with regard to the effect of the sulfur atom.

Mass Spectra.—Spectra were obtained with a Consolidated mass spectrometer, model 21–102.[26] Recommended procedures were followed in obtaining the spectra at an ionizing potential of 70 volts. Automatic controls maintained the catcher current (electron current to the collector) at 8.0 microamperes, and the temperature of the ionization chamber at 300°.

Ultraviolet Spectra.—The ultraviolet absorption spectra were determined with a Beckman quartz spectrophotometer, model DU, using matched silica sample cells 1.00 cm. in thickness. The solvent used for obtaining all of the spectra was 2,2,4-trimethylpentane, prepared by distilling "pure grade isoöctane" and then passing it through silica gel. The purified solvent was transparent down to 208 mμ. Data were taken at 1-mμ intervals except at inflection points, where readings were taken at 0.5-mμ intervals.

Infrared Spectra.—The infrared spectra were determined with a Perkin–Elmer spectrometer, model 12B. Spectra in the 2–15 μ region were obtained using a sodium chloride prism, and sample cells having sodium chloride windows. Spectra in the 14–25 μ region were obtained using a potassium bromide prism, and sample cells having potassium bromide windows. The spectra were calculated from point-by-point per cent. transmission measurements on the recorder tracing.

Discussion

Mass Spectra.—Abridged mass spectra of the compounds are presented in Table V. These spectra differ from those of hydrocarbons by the large number of peaks that cannot be explained by simple splitting of the molecule. One example of this is the mass 35 peak that was observed on several of the spectra and must result from a H_3S^+ particle. This suggests that, under the high-energy conditions in the mass spectrometer, the compounds rearrange so that three hydrogen atoms are associated with the sulfur atom at the time of splitting. Somewhat similar in showing the affinity of the sulfur atom for hydrogen are the rearrangement peaks of the disulfides. 3,4-Dithiahexane gives peaks corresponding to mass 66 ($HSSH^+$) and to mass 94 ($C_2H_5SSH^+$ or $CH_3SSCH_3^+$). 2,3-Dithiabutane has a peak at mass 48 (CH_3SH^+). Other rearrangement peaks include the mass 29 peak ($C_2H_5^+$) of 2-methyl-2-propanethiol; the mass 47 peaks (CH_2SH^+ or CH_3S^+) of 2-methyl-2-propanethiol, 3-thiapentane and thiacyclopentane; the mass 48 peak (CH_3SH^+) of 2-thiabutane; the mass 61 peak ($CH_3SCH_2^+$) of 2,3-dithiabutane; and the mass 62 peak ($C_2H_5SH^+$) of 3-thiapentane. All but one of these fragments include sulfur.

The most stable compounds to mass spectrometric breakdown are 2,3-dithiabutane and thiophene. Both compounds have, as their highest peak, the ion formed from the entire molecule. None of the other compounds have parent peaks of this magnitude. The sulfur–carbon bond appears to be particularly susceptible to cleavage, and large peaks often result from such splitting.

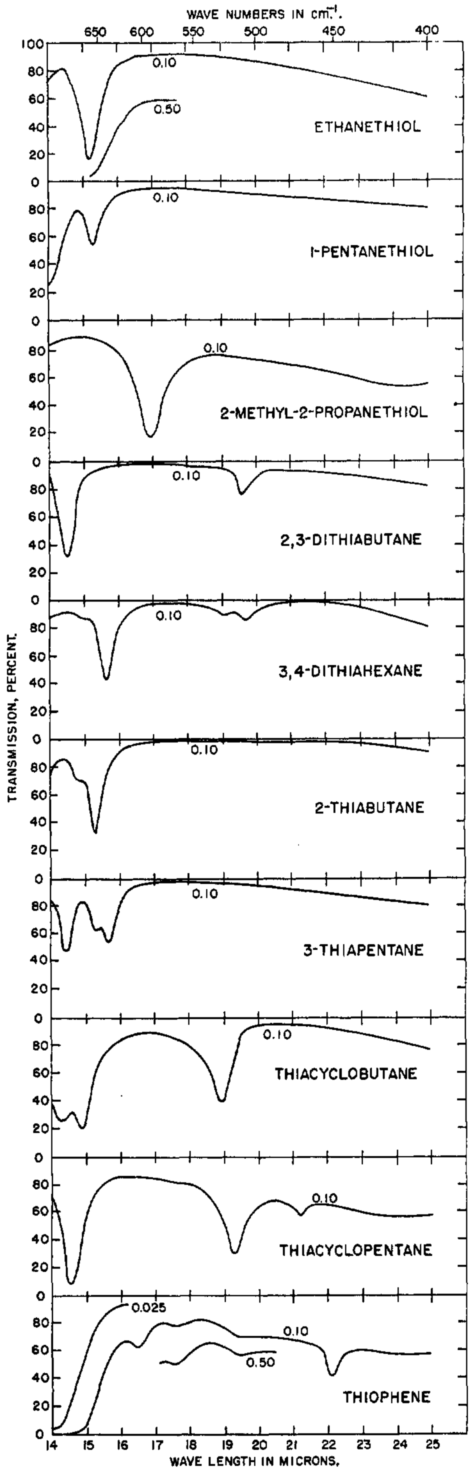

Fig. 4.—Infrared spectra (14–25 μ) of ten sulfur compounds.

Ultraviolet Spectra.—The ultraviolet absorption spectra of three thiols and two disulfides are shown in Fig. 1. The bands shown seem to be shoulders on more intense absorption maxima beyond the range of the instrument. The shoulder for ethanethiol and 2-methyl-2-propanethiol appears at 230 mμ, while for 1-pentanethiol it is displaced slightly toward shorter wave lengths (224 mμ). The two disulfides show similar bands but of

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(25) 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.

(26) H. W. Washburn, H. F. Wiley, S. M. Rock and C. E. Berry, *Ind. Eng. Chem., Anal. Ed.*, **15**, 541 (1943)

greater intensity and at longer wave lengths (250–256 mμ).

The ultraviolet absorption spectra of four sulfides and thiophene are shown in Fig. 2. The sulfides have narrow absorption bands of rather high intensity at about 215 mμ. The bands for the cyclic sulfides are displaced about 5 mμ toward longer wave lengths, are broader and reduced in intensity compared to the straight-chain sulfides. Fehnel and Carmack[27] observed shoulders in the region of 225–235 mμ in the spectra of some aliphatic sulfides and thiacyclohexane and noted that, in the spectrum of thiacyclopentane, this shoulder was shifted 10 mμ toward longer wave lengths. The curves in Fig. 2 confirm these observations and show, in addition, that the shoulder for thiacyclobutane is resolved into a broad band whose maximum is shifted still farther toward longer wave lengths (275 mμ).

The effect of the double bonds in the five-membered ring may be seen by comparing the spectrum of thiophene with that of thiacyclopentane. For thiophene, the band has been broadened, greatly intensified, and shifted toward longer wave lengths. The maximum for thiophene occurs at 231 mμ, with slight shoulders at 240 and 235 mμ.

Infrared Spectra.—The infrared spectra of all of the compounds are shown in Figs. 3 and 4. The cell lengths used are noted on each of the curves.

The three thiols exhibit characteristic absorption bands at 3.90 μ. These bands, due to an S–H stretching vibration, should be useful for detecting the presence of thiols in mixtures of sulfur compounds. The thiols also exhibit absorption bands between 11.0–12.2 μ which are probably due to a C–S–H bending vibration.[8]

All of the compounds except thiophene have rather intense bands attributed to C–S stretching vibrations in the region 13.0–15.5 μ. Although thiophene exhibits an extremely intense absorption band in this region (14.03 μ) this has been attributed to a symmetrical hydrogen bending mode wherein the hydrogen atoms vibrate in unison out of the plane of the nucleus.[28]

The two disulfides have medium bands at 19.6 μ which are probably attributable to S–S stretching vibrations. These bands are not very useful for detecting the presence of disulfides in mixtures of sulfur compounds because the three cyclic sulfur compounds also exhibit bands in this region (19.0–22.0 μ). These vibrations are probably due to a ring deformation.

The remaining bands in the spectra are caused by vibrations involving the C–H and C–C linkages in the hydrocarbon part of the molecules. Bending and rocking vibrations due to CH_3 and twisting and wagging vibrations of CH_2 are found in their usual regions, 7.2–13.6 μ. The band at about 3.40 μ in all of the compounds except thiophene is attributed to C–H stretching vibrations. This band in thiophene falls at 3.23 μ which is similar in location to that of terminal olefin groups.

More complete vibrational assignments have been made on several of these compounds in a series of papers presenting thermodynamic properties of the sulfur compounds.[8]

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

[28] H. D. Hartough, "Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 121.