Purification and Properties of Ten Organic Sulfur Compounds

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SEVEN THIOLS and three sulfides comprise the third series of compounds that have been prepared by American Petroleum Institute Research Project 48A. This project, cooperatively sponsored by the Bureau of Mines and the API, was established 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: common physical properties including density, refractive index, viscosity, surface tension, melting point, cryoscopic constant, and boiling point; reference spectra; and thermodynamic properties. Spectra and physical property data on 20 of these high-purity sulfur compounds have been published (*3, 4*). This article reports the physical properties and spectra of the following compounds: methanethiol, 1-propanethiol, 2-methyl-1-propanethiol, 2-methyl-2-butanethiol, 1-hexanethiol, benzenethiol, 1-heptanethiol, 2-thiahexane, 4-thiaheptane, and 5-thianonane. These purified compounds may be purchased from the API Samples and Data Office, Carnegie Institute of Technology. Thermodynamic properties have been reported separately for 1-propanethiol (*6, 7*) and benzenethiol (*9*).

PURIFICATION

To meet the needs of the standard sample and property program, approximately 1.5 liters of material with a purity of 99.9 mole % is required. The purification procedures were similar to those described in a previous article (*3*). Details of the purification procedures for individual compounds are given below. Distillations were made at atmospheric pressure (585 mm.) unless otherwise specified.

Methanethiol. Starting material for this purification was donated to the Project by Union Oil Co. of California. Because of the low boiling point of this compound (about 0° C. at Laramie atmospheric pressure), a specially designed apparatus was constructed for the distillation. The distillation pot was a 3-liter flask immersed to the neck in a water bath maintained near 0° C. A vacuum-jacketed columm with a 75 × 2.5 cm. section packed with glass helices was used. The liquid-dividing still head was carefully insulated, and the distillate condenser was cooled by circulating ethanol maintained at −50° C. Charge material was introduced to the pot through a phosphorus pentoxide drying system. Heat was supplied by an immersion heater placed in the thermometer well of the flask. Fractions were taken in borosilicate glass ampoules cooled in dry ice, and were immediately sealed. About 3 liters of charge material was distilled in this manner. Purities of the fractions were calculated from freezing point data, and the yield of high-purity (99.94 mole %) material was 1.6 liters.

1-Propanethiol. Starting material for the purification was 5 liters of 1-propanethiol from Eastman Kodak Co. This material was distilled through a Podbielniak Heligrid column with a 5-foot packed section (column 1). Approximately 1.5 liters of high-purity (99.93 mole %) material was obtained.

2-Methyl-1-propanethiol. About 4 liters of material was obtained from Columbia Organic Chemicals Co. and distilled through column 1. Because the compound did not crystallize, purity estimations on the fractions were made by mass spectral comparisons. From these comparisons the best fractions were combined to yield about 1.1 liters of high-purity material. A purity of 99.99 mole % was determined cryoscopically in the Thermodynamics Laboratory, Bureau of Mines, Bartlesville, Okla.

2-Methyl-2-butanethiol. Four liters of "*tert*-amyl mercaptan," donated by Phillips Petroleum Co., was distilled through an 8-foot by 1-inch Oldershaw column (column 2). Low-boiling impurities were separated, but mass spectral comparisons showed the presence of olefinic impurities in the fractions of highest purity. These fractions were combined with additional *tert*-amyl mercaptan, purchased from Phillips, and redistilled with purified 2-butanone (methyl ethyl ketone). Olefins were removed in the 2-butanone-olefin azeotrope, and the olefin-free thiol was then distilled. Freezing-point purity measurements could not be obtained on the fractions because of excessive supercooling before crystallization. Mass spectra, distillation data, and refractive indices of the fractions were used as criteria for combining fractions. Fractions amounting to 1.7 liters were combined and the purity (99.9 mole %) was determined in the Thermodynamics Laboratory, Bureau of Mines, Bartlesville, Okla.

1-Hexanethiol. Four kilograms, purchased from Columbia Organic Chemicals Co., was distilled at 200 mm. of mercury through a 7-foot by 1-inch Stedman-packed column (column 3). The best fractions as determined by freezing point were combined, yielding 2.4 liters of materials of about 99.8 mole % purity. The material was percolated through silica gel to remove olefins indicated by mass spectral data, and then redistilled through column 3 at 100 mm. The high-purity (99.9 mole %) material amounted to about 0.9 liter.

Benzenethiol. Four kilograms of material purchased from Eastman Kodak Co., was distilled through column 3 at 90 mm. of mercury. As freezing point data showed more than tolerable amounts of impurities, the best fractions were combined and redistilled. Highest-purity fractions from this distillation were combined to yield 1.4 liters of 99.98 mole % benzenethiol.

1-Heptanethiol. Five kilograms of 1-heptanethiol, from Columbia Organic Chemicals Co., was distilled through column 3 at reduced pressure (150 mm. of mercury). Purity measurements showed the need for further purification. Accordingly, the best fractions were combined and redistilled at a pressure of 100 mm. The highest-purity fractions, by freezing point data, were combined to yield 1.0 liter of material with a purity of 99.96 mole %.

2-Thiahexane. Four kilograms of this compound from Columbia Organic Chemicals Co. was distilled through column 1. Mass spectral comparisons indicated an unidentified impurity in uniform concentration in most of the fractions, suggesting that an azeotrope had been formed. These fractions were combined and redistilled with purified methyl Cellosolve, added as an entrainer for the azeotrope-forming impurity. The low-boiling azeotrope was removed and the later fractions were water-washed to remove methyl Cellosolve, then combined and redistilled. Based on freezing-point purity measurements, fractions were combined to yield 1.8 liters of 2-thiahexane with a purity of 99.9 mole %.

4-Thiaheptane. Four kilograms of material from Eastman Kodak Co. was distilled through column 3. The best fractions were combined and distilled through column 1, and 1.8 liters of high-purity (99.96 mole %) material was obtained.

5-Thianonane. Five kilograms was obtained from Eastman Kodak Co. and distilled through column 3 at a pressure of 40 mm. of mercury. Yield of high-purity (99.95 mole%) material was 1.1 liters.

STABILITY

Because a portion of each of these purified compounds is made available through the API Samples and Data Office to be used as calibration standards and for futher research, their storage stability is important and was investigated. Duplicate samples were sealed in vacuo in borosilicate glass ampoules. One of the duplicates was stored in the dark at room temperature for one year, and the other was exposed to sunlight on the laboratory roof for the same period of time. At the end of the test period the liquid samples were frozen in a suitable bath. The ampoules were then opened directly into the mass spectrometer, so that gaseous material could be analyzed. Small amounts of gaseous decomposition products were then detectable (*5*). Mass spectra of the stored liquids were also obtained for comparison with the spectra of the pure compounds; freezing point purities were determined if possible.

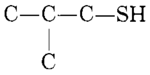
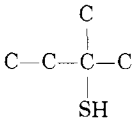
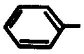
Comparison of the spectra and freezing points of the stored samples with those of the pure compounds permitted the estimation of the amouts of decomposition during storage. All of the samples stored in the dark compared favorably with the original purified material, showing no decomposition. Samples of methanethiol, 1-propanethiol, 2-methyl-1-propanethiol, and 4-thiaheptane stored on the roof also showed no decomposition. Small amounts of hydrogen were detected in the gas above the exposed samples of 2-methyl-2-butanethiol, 5-thianonane, 2-thiahexane, 1-hexanethiol, and 1-heptanethiol, indicating slight decomposition. Freezing point data on these compounds indicated the reduction in purity was less than 0.1 mole %. The sample of benzenethiol exposed on the roof showed extensive degradation. The gas above the sample was found to be 96 mole % hydrogen, and the remainer was hydrogen sulfide. Impurities in the liquid were estimated to be about 10 mole %, too great for reliable calculation from freezing point data. A study of the effects of light on this and other organic sulfur compounds has been reported separately (*5*).

Indications are that these samples, when sealed in vacuo and stored in the dark, will not deteriorate. Samples exposed to light may show some decomposition. No investigation was made of the effect of contact with air during storage.

PHYSICAL PROPERTIES

Physical property data for the ten organic sulfur compounds are shown in Tables I and II. The apparatus and procedures were described in a previous article (*3*), except for that used in the determination of the surface tension of benzenethiol. For this determination the maximum-bubble-pressure method and apparatus, as described by Quayle (*8*), was used. The capillary-rise method, used for measuring the surface tension of the other compounds in this series, was not suitable for studying benzenethiol because the high light dispersion of this compound prevented location of the miniscus. Monochromatic light sources failed to overcome this difficulty. The uncertainties in the tabulated values are as follows: Freezing point ±0.01°; boiling point, ±0.1°; refractive index, ±0.00006; density, ±0.00005 grams per ml.; viscosity, ±0.001 centipoise; and surface tension, ±0.1

Table I. Properties of Ten Organic Sulfur Compounds

Compd. No.	Skeleton Formula	Impurity, Mole %	F. P. for Zero Impurity, ° C.	Cryoscopic Constant, A, Deg.$^{-1}$	B. P. at 760 Mm., ° C.	Temp., ° C.	Density, G./Ml.	Viscosity, Cps.	Surface Tension, Dynes/Cm.
1	C—SH	0.06 ± 0.06	−122.97	...	5.9	[a]	[a]	[a]	[a]
2	C—C—C—SH	0.07 ± 0.07	−113.13	0.026	67.8	20	0.84150	0.399	24.7
						25	0.83616	0.377	24.0
						30	0.83084	0.359	23.5
3	 $\mathrm{C{-}\underset{\displaystyle C}{C}{-}C{-}SH}$	0.01 ± 0.01	−144.86	0.036	88.5	20	0.83428	0.506	24.1
						25	0.82931	0.477	23.4
						30	0.82435	0.451	23.0
4	 $\mathrm{C{-}C{-}\overset{\displaystyle C}{\underset{\displaystyle SH}{C}}{-}C}$	0.1 ± 0.1	−103.9[b]	0.0026[c]	99.2	20	0.82588	0.715	23.5
						25	0.82119	0.665	23.1
						30	0.81661	0.620	22.8
5	n—C_6—SH	0.1 ± 0.1	−80.49[b]	0.055[c]	152.6	20	0.84242	0.813	27.6
						25	0.83826	0.761	27.0
						30	0.83398	0.715	26.5
6	 SH	0.02 ± 0.02	−14.94	0.021	169.1	20	1.07758	1.239	39.5
						25	1.07276	1.144	38.7
						30	1.06811	1.058	38.0
7	n—C_7—SH	0.04 ± 0.02	−43.23[b]	0.058	176.9	20	0.84310	1.043	28.2
						25	0.83912	0.970	27.7
						30	0.83500	0.904	27.3
8	C—S—C—C—C—C	0.1 ± 0.1	−97.83	0.045	123.5	20	0.84230	0.594	26.4
						25	0.83779	0.562	25.9
						30	0.83314	0.528	25.4
9	C—C—C—S—C—C—C	0.04 ± 0.01	−102.71[b]	0.050[c]	142.7	20	0.83762	0.691	26.1
						25	0.83314	0.646	25.5
						30	0.82868	0.608	25.0
10	n—C_4—S—n—C_4	0.05 ± 0.05	−75.03	0.056	188.8	20	0.83849	1.054	27.1
						25	0.83442	0.978	26.6
						30	0.83033	0.908	26.2

[a] Measurements at 20°, 25°, and 30° C. are impossible at atmospheric pressure because of the low boiling point of this compound.

[b] Triple point measured by Thermodynamics Laboratory, Bartlesville, Okla.

[c] Measured by Thermodynamics Laboratory, Bartlesville, Okla.

dyne per cm. Properties for methanethiol were not obtained because of its low boiling point.

DERIVED FUNCTIONS

Two types of derived functions, additive and nonadditive, were calculated from the physical property data. Specific dispersion and refractivity intercept are nonadditive functions, used analytically to distinguish different classes of hydrocarbons. The additive or constitutive functions are molecular volume, molecular refraction, and parachor. Values for these functions calculated from data at 20° C. are shown in Table III.

Refractivity Intercept. This function has been used to estimate paraffins and naphthenes in petroleum fractions. Refractivity intercept values for paraffins are about 1.05, for naphthenes, about 1.03. If aliphatic sulfur compounds were present, they would be erroneously estimated as naphthenes, as can be seen from their low values reported in Table III.

Specific Dispersion. This function has been used to determine aromatics in straight-run petroleum fractions. Specific dispersion values for aliphatic sulfur compounds are about 10% higher than those of saturated hydrocarbons, (Table III). Presence of sulfur compounds in petroleum fractions will therefore lead to high estimations of the aromatic content.

Molecular Volume. The observed molecular volumes for the sulfur compounds are shown in Table III. An apparent volume for the sulfur atom can be obtained if the calculated molecular volume of the hydrocarbon portion of the molecule, using increments given in the review by Brooks and others (2), is subtracted from the observed values. This apparent volume varies, even within the same type of compounds. From the values for 1-propanethiol, an apparent sulfur volume of 10.47 ml. per mole is obtained, while from 1-heptanethiol the value is 11.72 ml. per mole, a difference of 1.25 ml. per mole. This difference may be attributed to deviations expected in the low molecular weight range. However, by similar calculations, the apparent sulfur volume in 2-thiahexane and 5-thianonane is 11.12 and 13.03, respectively, a difference of 1.91. In this higher molecular weight range, this difference is probably a reflection of the position of the sulfur within the molecule. In 2-methyl-2-butanethiol the apparent sulfur volume is 13.58, indicating the exaggerated effect of branching and of the sulfur position. Thus, it appears that the apparent volume of the sulfur atom is a function of other variables within the molecule and is not, in itself, a simple additive entity. When the molecular volume of the compound is multiplied by a suitable correction factor, the apparent sulfur increment may approach a constant value. Molecular refraction and parachor introduce such a correction factor.

Table II. Refractive Indices of Ten Organic Sulfur Compounds

No.	Compound	Temp., ° C.	Refractive Index						
			Helium *r* 6678.1 A.	Hydrogen *C* 6562.8 A.	Sodium *D* 5892.6 A.	Mercury *e* 5460.7 A.	Helium *v* 5015.7 A.	Hydrogen *F* 4861.3 A.	Mercury *g* 4358.3 A.
1	Methanethiol (methyl mercaptan)	[a]							
2	1-Propanethiol (*n*-propyl mercaptan)	20	1.43508	1.43549	1.43832	1.44074	1.44396	1.44530	1.45098
		25	1.43214	1.43253	1.43534	1.43777	1.44095	1.44231	1.44793
		30	1.42914	1.42957	1.43236	1.43475	1.43793	1.43928	1.44484
3	2-Methyl-1-propanethiol (isobutyl mercaptan)	20	1.43566	1.43606	1.43877	1.44114	1.44427	1.44551	1.45098
		25	1.43289	1.43329	1.43603	1.43833	1.44141	1.44274	1.44812
		30	1.43009	1.43051	1.43321	1.43549	1.43856	1.43986	1.44522
4	2-Methyl-2-butanethiol (*tert*-amyl mercaptan)	20	1.43500	1.43539	1.43813	1.44037	1.44340	1.44472	1.45015
		25	1.43230	1.43268	1.43535	1.43765	1.44074	1.44197	1.44732
		30	1.42963	1.43004	1.43265	1.43496	1.43805	1.43928	1.44458
5	1-Hexanethiol (*n*-hexyl mercaptan)	20	1.44668	1.44704	1.44968	1.45199	1.45507	1.45632	1.46160
		25	1.44423	1.44459	1.44728	1.44953	1.45257	1.45384	1.45913
		30	1.44186	1.44223	1.44486	1.44715	1.45018	1.45140	1.45665
6	Benzenethiol (thiophenol)	20	1.58267	1.58356	1.59008	1.59580	1.60365	1.60691	1.62134
		25	1.57983	1.58076	1.58722	1.59288	1.60066	1.60404	1.61827
		30	1.57699	1.57789	1.58429	1.58994	1.59770	1.60103	1.61519
7	1-Heptanethiol (*n*-heptyl mercaptan)	20	1.44909	1.44950	1.45215	1.45441	1.45741	1.45868	1.46393
		25	1.44682	1.44717	1.44981	1.45204	1.45509	1.45634	1.46150
		30	1.44450	1.44487	1.44748	1.44974	1.45272	1.45396	1.45911
8	2-Thiahezane (methyl *n*-butyl sulfide)	20	1.44464	1.44506	1.44781	1.45017	1.45329	1.45465	1.46006
		25	1.44210	1.44253	1.44527	1.44759	1.45067	1.45205	1.45744
		30	1.43958	1.43999	1.44271	1.44502	1.44811	1.44944	1.45484
9	4-Thiaheptane (di-*n*-propyl sulfide)	20	1.44563	1.44602	1.44877	1.45100	1.45414	1.45546	1.46084
		25	1.44312	1.44349	1.44623	1.44854	1.45160	1.45289	1.45824
		30	1.44061	1.44098	1.44372	1.44597	1.44902	1.45026	1.45561
10	5-Thianonane (di-*n*-butyl sulfide)	20	1.44987	1.45024	1.45293	1.45517	1.45821	1.45946	1.46470
		25	1.44754	1.44797	1.45062	1.45284	1.45586	1.45714	1.46233
		30	1.44522	1.44563	1.44827	1.45050	1.45351	1.45476	1.45993

[a] Measurements at 20°, 25°, and 30° C. are impossible at atmospsheric pressure because of the low boiling point of this compound.

Table III. Derived Functions

Compound	Refractivity Intercept[a]	Specific Dispersion[b]	Molecular Volume[c]	Parachor Obsd.[d]	Parachor Sugden (*10*)	Parachor M.&P. (*10*)	Molecular Refraction Obsd[e]	Molecular Refraction H—C Portion Calcd. (*10*)	Molecular Refraction Additive Sulfur Increment
Methanethiol	...	...	...	...	...	...	...	...	...
1-Propanethiol	1.01057	116.6	90.51	201.9	199.4	200.8	23.78	16.12	7.66
2-Methyl-1-propanethiol	1.02163	113.3	108.10	239.6	238.4	240.8	28.42	20.76	7.66
2-Methyl-2-butanethiol	1.02519	113.0	126.18	277.9	277.4	280.8	33.14	25.40	7.74
1-Hexanethiol	1.02847	110.2	140.36	321.7	316.4	320.8	37.70	30.04	7.66
Benzenethiol	1.05129	216.7	102.24	256.5	255.3	255.4	34.51	26.31	8.20
1-Heptanethiol	1.03060	108.9	156.88	361.5	355.4	360.8	42.33	34.68	7.65
2-Thiahexane	1.02666	113.9	123.72	280.5	277.4	280.8	33.11	25.40	7.71
4-Thiaheptane	1.02996	112.7	141.16	319.1	316.4	320.8	37.84	30.04	7.80
5-Thianonane	1.03368	110.0	174.47	398.1	394.4	400.8	47.16	39.32	7.84

[a] Refractivity intercept $= n_D^{20} - \frac{d_4^{20}}{2}$

[b] Specific dispersion $= \frac{(n_F^{20} - n_C^{20})\,10^4}{d_4^{20}}$

[c] Molecular volume $= \frac{M}{d_4^{20}}$

[d] Parachor $= \frac{M\gamma^{1/4}}{d_{liq.} - d_{vap.}}$

[e] Molecular refraction $= \frac{M[(n_D^{20})^2 - 1]}{d[(n_D^{20})^2 + 2]}$

Molecular Refraction. Molecular refraction is molecular volume multiplied by a function of the refractive index. Sulfur increments, shown in Table III, were calculated using the hydrocarbon increments for molecular refraction as given in the review by Brooks and others (*2*). The calculated molecular refraction value of the hydrocarbon skeleton was substracted from the observed molecular refraction of the sulfur compound.

A molecular-refraction increment of 7.8 ±0.2 ml. per mole for the sulfur atom in aliphatic thiols has been proposed (*3*). The present data for aliphatic thiols support this increment. The increment for sulfides, while slightly higher, also falls within these limits.

Parachor. Parachor is a function of molecular volume and surface tension. Values for parachor are given in Table III, and included for comparison are values calculated from the increments of Sugden, and of Mumford and Phillips (*10*). The Mumford and Phillips values agree with the observed parachors within 1%. Values calculated using Sugden's increments are low, by as much as 2%.

SPECTRA

Mass, ultraviolet, and infrared spectra were determined on each of the ten compounds. The mass spectra were obtained with a Consolidated mass spectrometer, Model 21-103 (21-102 modified). The ultraviolet spectra were obtained with a Cary ultraviolet spectrophotometer, Model 11. The infrared spectra were obtained with a Perkin-Elmer Model 12C spectrometer. Operating conditions are given elsewhere (*3*). Complete spectra are included in the Catalogs of Spectral Data (*1*).

Mass Spectra. Abridged mass spectra of the compounds are presented in Table IV. The influence of the sulfur atom on the spectra is evident from the abundance of ions containing this atom. The peaks at *m/e's* 32-35, 45-47, 61, and 75 are due to sulfur-containing ions. For some of the compounds these peaks are large, even though they must be formed by rearrangement rather than simple cleavage of bonds. The abundance of rearrangement peaks in thiol and sulfide spectra has been pointed out (*3, 4*).

The chain fragments from the higher molecular weight compounds form a pattern that resembles olefins. The thiols and sulfides have large peaks at *m/e*'s 41, 42, 55, 56, 69, and 70, which are typical of olefins.

Benzenethiol has a spectrum that is typical of a low molecular weight aromatic compound, with the most abundant ion at the molecular weight of the compound. The large peak at *m/e*'s 39, 50, 51, 66, 76, and 77 are usual in the spectra of aromatics. The peak at *m/e* 95 is unusual in that it requires the loss of 15 mass units from the parent molecule. Careful investigation indicated that the peak was not due to an impurity.

Ultraviolet Spectra. One of the compounds, methanethiol, is a gas at room temperature. To overcome the difficulties of weighing a sample of this material, an approximate amount was placed in solution in cyclohexane. The resulting mixture was analyzed mass spectrometrically and by titration with silver nitrate. The results agreed within ±0.05 gram per liter. To avoid errors from selective evaporation, the ultraviolet spectrum and the analyses were obtained simultaneously on aliquots of the solution.

The spectra of the aliphatic thiols show single, broad absorption bands at 2250 to 2300 A. with molar absorptivities between 135 and 160. The sulfides have ill-defined bands near 2150 A. and weak shoulders at 2250 to 2350 A. The molar absoptivities, ϵ, of the bands are about 1000 and the shoulders about 100. These results are similar to those previously reported (*3, 4*).

The spectrum of benzenethiol has a band at 2360 A., ϵ = 8390, a shoulder at 2540 A., ϵ = 2600, a band at 2700-2730 A., ϵ = 650, a band at 2800 A., ϵ = 615, and a band at 2875 A., ϵ = 405.

Infrared Spectra. A medium intensity band appears in the spectra of all ten compounds between 15 and 16.2 microns. This is presumed to be the C—S stretching vibration for the thiols and sulfides, which has been reported to be in the 13 to 15.5 micron region. For some of the compounds geometrical isomerism may cause additional absorption bands in the region due to the C—S stretching vibration. This has been discussed, and assignments have been made for 1-propanethiol (*7*).

The spectrum of benzenethiol in the 5 to 6 micron region is typical of a monosubstituted benzene as shown by Young, Duvall, and Wright (*11*). The C—H out-of-plane bending vibrations are near 13.5 and 14.5 microns. The S—H stretching vibration is at the expected position of 3.9 microns. However, the intensity of the vibration is greatly enhanced compared with the alkanethiols. Vibrational assignments have been made for benzenethiol (*9*).

The spectrum of methanethiol was obtained on the gas. It shows an S—H stretching vibration at 3.8 microns. Additional absorption maxima occur near 6.8, 7.5, 9.3, 12.5, and 14 microns. The first three regions contain two bands and the last two regions have three bands. The usual C—H stretching vibration is evident near 3.5 microns.

Table IV. Mass Spectra.

	Relative Intensity									
Mass No. *m/e*	5-Thia-nonane M.W. = 146	4-Thia-heptane M.W. = 118	2-Thia-hexane M.W. = 104	Benzene-thiol M.W. = 110	1-Heptane-thiol M.W. = 132	1-Hexane-thiol M.W. = 118	2-Methyl-2-butanethiol M.W. = 104	2-Methyl-1-propanethiol M.W. = 90	1-propane-thiol M.W. = 76	Methane-thiol M.W. = 48
15	2.55	7.72	7.63	1.84	6.23	5.32	8.32	9.59	13.2	13.7
27	41.2	63.3	43.5	6.04	82.0	60.6	36.9	43.3	78.9	...
29	58.8	11.0	32.0	0.20	67.5	38.9	29.4	26.2	9.07	...
32	0.16	0.46	0.44	3.93	1.33	1.20	2.40	1.64	5.62	11.6
33	0.18	0.43	0.45	5.15	3.44	3.22	6.89	3.93	12.1	12.1
34	0.43	0.67	0.51	1.83	4.00	2.99	3.45	2.04	5.28	2.40
35	2.19	1.16	10.4	0.27	7.51	5.82	1.31	1.39	10.9	0.58
39	16.1	33.0	16.7	24.5	45.0	30.6	34.5	38.5	38.7	...
41	45.8	66.1	50.5	0.41	100.0	62.3	52.5	100.0	74.9	...
42	3.27	60.5	2.38	0.20	61.5	38.9	6.53	11.6	72.9	...
43	5.19	100.0	2.26	0.22	55.9	56.7	100.0	77.2	79.6	...
44	0.09	3.33	0.58	0.30	1.78	1.89	3.32	2.63	4.35	12.6
45	12.8	26.3	23.4	16.7	19.1	15.0	7.49	21.9	34.5	61.4
46	8.61	17.5	12.9	0.53	7.55	6.14	0.95	16.1	25.9	14.7
47	21.4	61.9	26.6	0.94	46.2	32.6	11.3	48.5	100.0	100.0
48	2.52	4.52	24.3	0.46	2.46	2.17	0.37	35.7	11.0	75.8
49	2.22	3.80	15.9	3.19	2.35	1.78	1.12	11.6	4.58	...
50	0.53	0.25	2.49	17.4	1.37	1.32	2.29	3.36	0.44	...
51	0.85	0.15	2.06	21.9	2.49	2.07	3.15	2.09	...	...
55	23.9	6.61	10.4	4.67	69.8	41.9	39.0	10.1	...	...
56	91.0	0.78	65.1	0.70	81.3	100.0	2.78	56.7	0.41	...
57	31.1	0.74	13.2	5.51	29.2	7.02	0.94	23.7	3.08	...
58	2.27	3.83	3.55	6.52	3.32	2.82	3.61	2.82	6.79	...
59	3.93	4.64	5.05	1.67	5.16	3.95	11.8	3.17	5.22	...
60	4.79	2.39	1.69	0.89	5.07	3.43	0.88	0.79	1.21	...
61	100.0	36.0	100.0	2.83	19.1	14.3	3.04	2.16	10.7	...
62	4.04	1.42	12.3	3.46	1.66	1.35	0.41	0.13	0.37	...
65	0.05	0.03	0.05	14.4	0.83	0.46	0.28	0.02	...	...
66				37.5	0.33	0.15	0.11	0.02	...	...
68	0.05	0.07	0.05	1.02	14.4	0.89	0.11	0.26	0.77	...
69	0.46	0.76	0.42	16.7	43.5	22.3	1.27	1.50	2.41	...
70	0.23	0.12	0.12	1.86	79.2	1.68	2.74	0.19	0.27	...
71	0.57	1.59	0.75	3.58	5.65	0.79	61.7	1.78	1.37	...
75	3.78	12.3	17.0	2.73	0.97	0.50	26.7	6.52	0.97	...
76	0.31	48.3	1.26	2.08	0.18	0.13	1.20	0.52	70.4	...
77	0.19	11.2	0.81	17.2	0.36	0.18	1.20	0.30	...	...
84	0.06	0.03	0.06	19.2	0.54	11.6	...	0.05	...	...
89	11.5	85.8	4.41	...	6.63	2.86	2.63	0.77	...	...
90	23.1	4.74	0.24	...	0.33	0.18	0.13	57.8	...	...
91	10.6	3.86	0.21	...	0.33	0.18	0.15	...	...	...
95	...	...	...	2.30	0.06	...	...	...	...	...
98	...	0.01	...	...	13.9	...	...	...	...	...
103	12.9	2.00	0.52	...	0.42	...	...	...	...	...
104	...	...	49.0	...	0.11	...	21.1	...	...	...
110	...	...	...	100.0	...	...	...	...	...	...
117	5.09	0.57	...	...	...	0.48	...	...	...	...
118	0.39	54.7	...	...	...	24.5	...	...	...	...
132	...	...	...	...	28.2	...	...	...	...	...
146	31.1	...	...	...	...	...	...	...	...	...

ACKNOWLEDGMENT

The authors extend thanks to R. A. Meyer and F. M. Church for assistance in obtaining spectra, and to A. W. Decora for purification work on methanethiol.

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RECEIVED for review February 13, 1959. Accepted May 8, 1959. Investigation carried out as part of API Research Project 48A on the Synthesis, Properties, and Isolation of the Sulfur Compounds of Petroleum, conducted by the Bureau of Mines, U. S. Department of the Interior, at Laramie, Wyoming, and Bartlesville, Okla. Work done under a cooperative agreement between the Bureau of Mines and the University of Wyoming.