

the amide molecules. Thus the data are consistent with the idea that the degree of association is greatest for formamide, less for acetamide, and least for the next higher homologs.

A few binary mixtures of palmitic acid with malonamide, succinimide, cyanoacetamide and urea were investigated and found to form two liquid layers. The compositions studied were 40 and 70% of malonamide, 50% of succinimide, 10.5, 20, 50,

and 80% of cyanoacetamide, and 15, 22, 30, 40, 50, 60, 70 and 80% of urea. No freezing point data were obtained for these systems.

In none of the thirteen systems investigated was there separation of a crystalline molecular compound of palmitic acid with the amide, such as was previously found for acetamide. In this respect, therefore, acetamide seems to be unique.

NEW ORLEANS 19, LOUISIANA

[CONTRIBUTION NO. 24 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Thiacyclopropane (Ethylene Sulfide): Infrared Spectrum, Vapor Pressure and Some Thermodynamic Properties¹

BY G. B. GUTHRIE, JR., D. W. SCOTT AND GUY WADDINGTON

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The infrared spectrum of liquid thiacyclopropane (ethylene sulfide) was observed between 2 and 15 μ . Interpretation of the infrared data and other available spectroscopic data with the aid of normal coordinate calculations resulted in the following vibrational assignment: 625, 660, 824, 875, 943, 1025, 1051, 1100, 1112, 1427, 1446, 3000 (2) and 3080 (2). This assignment and moments of inertia from microwave measurements (ref. 13) were used to compute thermodynamic functions to 1000°K. The vapor pressure of thiacyclopropane was measured from 18 to 88° and the following equation was selected to represent the data: $\log_{10} p(\text{mm.}) = 7.03725 - 1194.37/(t + 232.42)$. The heat of vaporization at 25° calculated from this equation is 7240 ± 50 cal. mole⁻¹. The heat, free energy and equilibrium constant of formation of thiacyclopropane at selected temperatures to 1000°K. were computed using heat of combustion data for the liquid (ref. 2), the heat of vaporization and the thermodynamic functions.

The series of thiacycloalkanes (saturated cyclic sulfides) constitute one group of compounds in the thermodynamic research program of American Petroleum Institute Research Project 48A. Several members of this series and their derivatives have been identified in petroleum and others may be of interest to petroleum refiners and the chemical industry at large.

This paper presents the results of a study of the first member of the series, thiacyclopropane (ethylene sulfide). Since thiacyclopropane polymerizes readily, the experimental determination of its entropy and vapor heat capacity would have presented great practical difficulties and such measurements were not undertaken. However the relative simplicity of the molecule made it possible to obtain a reliable vibrational assignment and to circumvent these calorimetric measurements by calculating the thermodynamic functions from spectroscopic and molecular structure data alone. A value of the heat of formation of liquid thiacyclopropane was available from the work of Sunner,² but an accurate value of the heat of vaporization was necessary for extending this datum to the vapor state. The present investigation therefore included: (a) obtaining certain spectroscopic data not available in the literature and making a vibrational assignment, (b) obtaining a value of the heat of vaporization from a study of the vapor pressure as a function of temperature and (c) using the results of these studies and other available data to calculate the thermodynamic functions and

the heat, free energy and equilibrium constant of formation of thiacyclopropane for selected temperatures up to 1000°K.

When the present research was undertaken, the only spectroscopic data available for making a vibrational assignment were those of Thompson and Dupré,³ who had studied the Raman spectrum of the liquid and the infrared spectrum of the vapor, and had proposed a nearly complete vibrational assignment. Examination of these spectroscopic data and the proposed assignment suggested that some of the reported infrared bands may have been spurious and that other bands were obscured by the rotational structure of adjacent bands. For this reason, the infrared spectrum of thiacyclopropane was studied over the range 2–15 μ in the liquid state so that the bands would be sharpened and the conditions for resolving adjacent bands would be improved. The infrared spectrum of the polymerized material also was measured so that weak bands resulting from traces of polymer in the sample of thiacyclopropane could be identified. These studies revealed two previously unresolved bands in the region of fundamental frequencies and many new overtone and combination bands, and also confirmed the surmise that some of the bands observed by Thompson and Dupré were not characteristic of the pure substance. Shortly after these studies had been carried out in this Laboratory, Thompson and Cave⁴ published the results of a reinvestigation of the infrared spectrum of the vapor and the Raman spectrum of the liquid. They found that one of the strong bands reported by Thompson and Dupré had been due to hydrogen cyanide impurity. Also, by using infrared spectrometers of greater resolving power,

(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) S. Sunner, Dissertation, University of Lund, 1949, "Studies in Combustion Calorimetry Applied to Organo-sulfur Compounds," Carl Bloms Boktryckerie, Lund, Sweden, 1949, p. 76.

(3) H. W. Thompson and D. J. Dupré, *Trans. Faraday Soc.*, **36**, 805 (1940).

(4) H. W. Thompson and W. T. Cave, *ibid.*, **47**, 951 (1951).

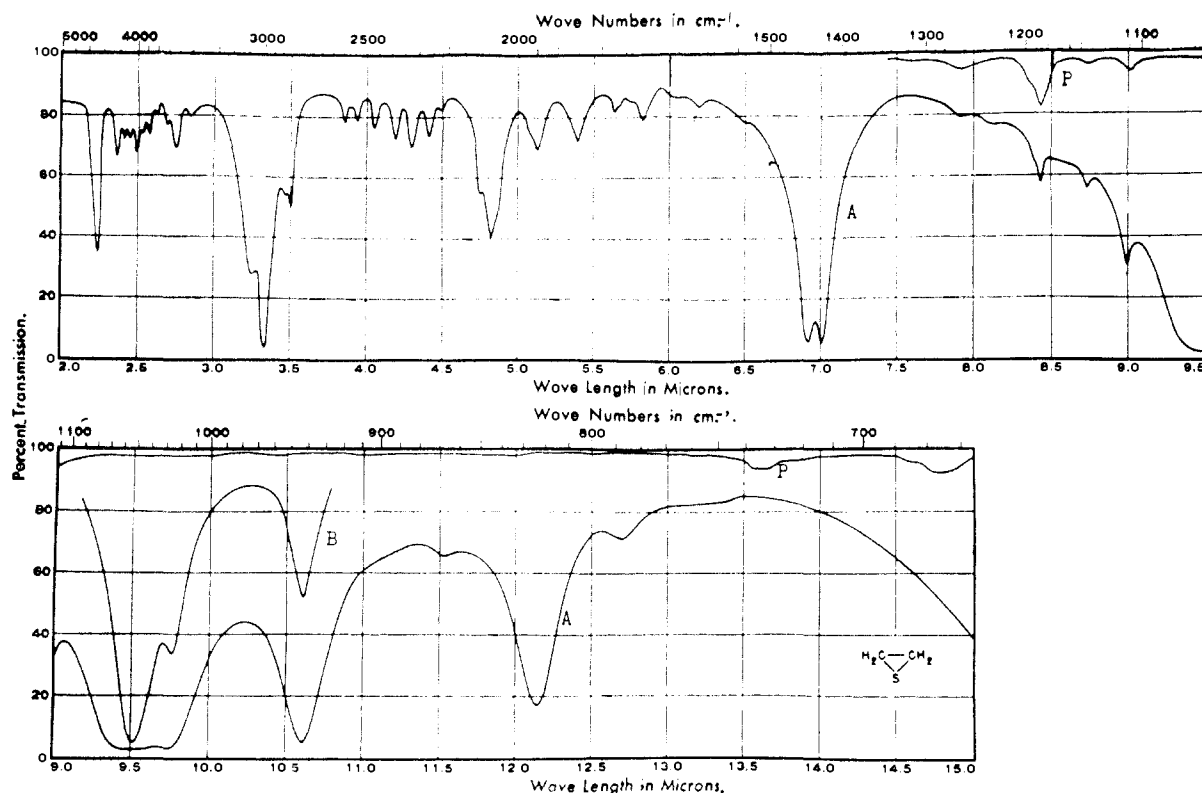


Fig. 1.—Spectra of thiacyclopropane and its polymer. A, monomer (liquid) cell thickness, 0.10 mm.; B, monomer (liquid) cell thickness, 0.025 mm.; P, polymer (nujol mull).

they observed much better defined contours for most of the bands than in the earlier work.

With the infrared data for the liquid obtained in this research and the recent data of Thompson and Cave, it was possible to make definite assignments for all but two of the thermodynamically important vibrational frequencies (*i.e.* those below 1500 cm^{-1}). The remaining two frequencies were estimated closely enough for purposes of thermodynamic calculations by means of a normal coordinate treatment.

Experimental

The Material.—The thiacyclopropane used for infrared and vapor pressure measurements was part of a sample prepared and purified by Experiment Incorporated of Richmond, Va.⁵ The purity of the material was not estimated quantitatively. Repurification was limited to separation of the monomer from the polymerized material by bulb-to-bulb distillation and to drying by passing the vapor over anhydrous magnesium perchlorate.

Polymerized thiacyclopropane which had precipitated from the original sample was collected on a fritted-glass filter. The polymer was washed several times with petroleum ether and dried for half an hour in a vacuum desiccator. The product was a white, odorless solid.

Infrared Measurements.⁶—Infrared measurements were made with a Perkin-Elmer infrared spectrometer model 12-A with a General Motors breaker-type D.C. amplifier, Brown Electronic recorder and power regulators. The Globar was operated at 200 watts. Slit widths were changed stepwise with actual slits of 0.85 mm. at 15 μ , 0.24

mm. at 10 μ and 0.01 mm. at 3 μ . The effects of stray radiation were minimized by using shutters of LiF (15 to 9.5 μ), glass (9.5 to 5 μ) and opaque material (5 to 2 μ). Two cell thicknesses were used. The probable error of wave length determination is $\pm 0.01 \mu$ (15 to 6 μ) and $\pm 0.02 \mu$ (6 to 2 μ).

To minimize polymerization, the freshly dried and distilled compound was placed in a sealed bulb under its own vapor pressure and kept at the temperature of solid carbon dioxide until shortly before the cell was filled. The cell was cleaned and refilled several times during the interval of about two hours required to obtain the spectrum. In spite of these precautions, several weak absorption bands probably due to polymer were observed.

The infrared spectrum of the polymerized thiacyclopropane was determined in a nujol mull.

The spectra of liquid thiacyclopropane from 2 to 15 μ and of polymerized thiacyclopropane from 7 to 15 μ are shown in Fig. 1. The positions of the absorption maxima are listed in Table I, along with the Raman and infrared data of Thompson and Cave.⁴ Comparison of the present with the other work shows that the absorption bands of the vapor reported at 685, 954, 970, 2410 and 2493 cm^{-1} are absent in the liquid spectrum and that the bands at 685 and 1270 cm^{-1} coincide with bands found in the polymer. It should be noted that the band reported at 685 cm^{-1} does not have the fine structure shown by the neighboring band. It is quite probable that this band was due to polymer on the window of the cell. Evidence of polymer is shown in the present work by the presence of the 1112-, 1145-, 1186- and 1263- cm^{-1} bands in both the liquid and polymer. The relative intensity of these bands in the two spectra suggests that the 1112- and 1145- cm^{-1} bands may originate in part from the monomer.⁷ Except for the above, the differences between the present spectrum and the previous work are

(5) Submitted by Dr. E. J. Wilson, Jr., for heat of combustion studies.

(6) These measurements were made by N. G. Adams and Dorothy Richardson of the Chemistry and Refining Branch of this Station. The spectrogram of liquid thiacyclopropane has been included in the "Catalog of Infrared Spectral Data," American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, 1951. Serial No. 1236.

(7) The section of the spectrum in which these bands were found was covered in a continuous recording. The entire section was traversed in three minutes, and the wave length decreased with time. If the amount of polymer changed during this run, it ordinarily would be expected to increase with increasing wave number. There is a possibility that polymer was precipitating out of the absorbing volume more rapidly than it was formed so that the relative intensity decreased with increasing wave number.

TABLE I
 SPECTRA OF THIACYCLOPROPANE

Raman ^a liquid, cm. ⁻¹	Infrared ^a vapor, cm. ⁻¹	Infrared ^b polymer, cm. ⁻¹	Infrared ^b liquid, cm. ⁻¹	Assignment
625 p	626			A ₁ Fundamental
660				B ₁ Fundamental
	685	671		Polymer
		725 } 738 }		Polymer
			786	1446 - 660 = 786 (B ₁)
827	825		824	B ₂ Fundamental
			866	?
	892 ?			?
941	945		943	B ₂ Fundamental
	954			?
	970			?
1040 p?	1050		1025	A ₁ Fundamental
			1051	B ₁ Fundamental
1120 p	1107	1110	1112	{ A ₁ Fundamental Polymer
		1144	1145	Polymer, ?
	1174	1185 } 1197 }	1186	Polymer
			1230	?
	1270 ?	1264	1263	Polymer
	1440		1427	B ₁ Fundamental
1450 p	1471		1446	A ₁ Fundamental
			1542 ?	?
			1615	?
			ca. 1655	{ 625 + 1025 = 1650 (A ₁) 2(824) = 1648 (A ₁)
			1717	1051 + 660 = 1711 (A ₁)
			ca. 1739	625 + 1112 = 1737 (A ₁)
			1771	660 + 1112 = 1772 (B ₁)
			1852	824 + 1025 = 1849 (B ₂)
			1949	?
			1972	943 + 1025 = 1968 (B ₂)
			2046	2(1025) = 2050 (A ₁)
	2074		2072	625 + 1446 = 2071 (A ₁), 1025 + 1051 = 2076 (B ₁)
			2102	2(1051) = 2102 (A ₁), 660 + 1446 = 2106 (B ₁)
			2224	2(1112) = 2224 (A ₁)
			2268	824 + 1446 = 2270 (B ₂)
			2333	3000 - 660 = 2340 (A ₁ or B ₁)
			2385	943 + 1446 = 2389 (B ₂)
	2410		3080 - 660 = 2420 (B ₂)	
			2468	1025 + 1446 = 2471 (A ₁)
	2493			1060 + 1446 = 2506 (B ₁)
			2541	1112 + 1427 = 2539 (B ₁)
	2594		2593	Ternary combinations
			2854	2(1427) = 2854 (A ₁)
2890	2898		2883	{ 1427 + 1446 = 2873 (B ₁) 2(1446) = 2892 (A ₁)
3010 p	3017		2995	A ₁ and B ₁ Fundamentals
3085	3089		3076	A ₂ and B ₂ Fundamentals

^a Reference 4, polarization data of ref. 3. ^b This research.

only those expected between liquid and vapor spectra. None of the Raman lines reported by Thompson and Cave⁴ seem to be attributable to polymer.

Vapor Pressure Measurements.—The vapor pressure of thiacyclopropane was studied by the ebulliometric method described in a previous publication from this Laboratory.⁸ The differential feature of the ebulliometer, by means of which both the boiling and condensation temperatures were measured, was particularly advantageous for the study of a

compound such as this which readily forms non-volatile polymer. The rate of polymerization was reduced during the course of measurements by the addition of a retarder of negligible volatility.⁹ The dissolved polymer and retarder depressed the boiling temperature of the sample, but these solutes, being essentially non-volatile, did not have any significant effect on the condensation temperature. This was then taken as the vapor-liquid equilibrium temperature of the sample not containing polymer or retarder.

(8) G. Waddington, J. W. Knowlton, D. W. Scott, G. D. Oliver, S. S. Todd, W. N. Hubbard, J. C. Smith and H. M. Huffman, *This Journal*, **71**, 797 (1949).

(9) According to W. Coltof and S. L. Langedijk, U. S. Patent 2,185,660, most divalent sulfur compounds are suitable retarders of the polymerization of thiacyclopropane.

The retarder used was 1,3,5-trithiacyclohexane (trithiane); approximately 0.2 g. of this material was added to the sample in the ebullimeter. In addition, a small amount of thia- β -naphthol (which had been used to stabilize the sample during storage) was inadvertently introduced as the result of bumping while the sample was being distilled into the ebullimeter. Only a small fraction of the thiacyclopropane containing these retarders polymerized in the three-day period required for measurements.

The difference between the boiling and condensation temperatures of the sample containing dissolved polymer and added retarder could not be used as a criterion of purity. Instead, a qualitative indication of purity was obtained by making duplicate series of measurements, the first with 80 ml. of the compound in the ebullimeter and the second after half of this amount had been distilled out. For a pure sample, the condensation temperature would be unchanged by distilling out a portion of the sample. Actually the observed condensation temperatures were higher by 0.03 to 0.05° in the second series than in the first. For example, at 1 atm. pressure the condensation temperatures were 54.917° for the first series and 54.950° for the second. These results show that the sample contained a small but significant amount of impurity of different volatility. However, this impurity does not have a significant effect on the heat of vaporization calculated from these vapor pressure data since the values of $d \ln p/d(1/T)$ obtained from the two series are essentially identical.

The results of the vapor pressure measurements are summarized in Table II. The condensation temperatures listed in the second column are the averages of the values for the two series and have been rounded off to the nearest hundredth degree. The Antoine equation, $\log_{10} p = A + B/(t + C)$, which has been fitted to these vapor pressure data by a least-squares adjustment,¹⁰ is

$$\log_{10} p = 7.03725 - 1194.37/(t + 232.42) \quad (1)$$

The B and C constants of this equation are given to one less than the customary number of decimal places, because the data on which the equation is based are necessarily somewhat less accurate than those usually obtained in this Laboratory with carefully purified samples of stable compounds. Values of the vapor pressure computed by means of eq. 1 are given in column 4 of Table II for comparison with the observed values in column 3.

TABLE II
VAPOR PRESSURE OF THIACYCLOPROPANE

Boiling temp. of water, °C.	Condensation temp. of sample, °C.	Vapor pressure, mm.	
		Obsd.	Calcd. (eq. 1)
65.00	18.29	187.58	187.63
70	23.41	233.72	233.69
75	28.58	289.13	289.15
80	33.78	355.22	355.23
85	39.01	433.56	433.47
90	44.29	525.86	525.93
95	49.59	633.99	633.95
100	54.93	760.00	759.89
105	60.31	906.06	906.02
110	65.72	1074.6	1074.4
115	71.12	1268.0	1268.3
120	76.66	1489.1	1489.3
125	82.18	1740.8	1740.9
130	87.73	2026.0	2025.8

The heat of vaporization at 298.16°K. was computed from the vapor pressure data by means of the Clapeyron equation. Since neither the equation of state nor values of the critical constants of thiacyclopropane were available, the molal volume of the saturated vapor was estimated empirically. The equation of state $PV = RT + BP$, with the second virial coefficient B having the value -0.85 l. at 298.16°K., was used. This value of the second virial coefficient was estimated by means of a correlation similar to

(10) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *J. Research Natl. Bur. Standards*, **56**, 219 (1945).

that described previously,¹¹ but based on second virial coefficient data for nine sulfur compounds. The calculated value of the heat of vaporization at 298.16°K. is 7240 cal. mole⁻¹ with an estimated uncertainty of ± 50 cal. mole⁻¹.

Vibrational Assignment

Direct Assignment from Spectroscopic Data.—

The assignment of the observed fundamental frequencies of thiacyclopropane adopted here differs in only a few respects from that of Thompson and Cave.⁴ The following frequencies, all of which appear with at least moderate intensity in one or both spectra, were selected as the observed fundamentals: 625, 660, 824, 943, 1025, 1051, 1112, 1427, 1446, 3000 and 3080 cm.⁻¹. The principal differences between the above values and those given by Thompson and Cave are the omission of the infrared band at 686 cm.⁻¹ (attributed to polymer) and the inclusion of the infrared band at 1025 cm.⁻¹. The latter appears as a rather strong band in the spectrum of the liquid but is obscured in the spectrum of the vapor by the stronger and extremely broad band at 1050 cm.⁻¹.

The thiacyclopropane molecule has C_{2v} point group symmetry, and its vibrations fall into the four symmetry classes A_1 , B_1 , B_2 and A_2 , the first three of which are active in both spectra and the fourth only in the Raman spectrum. The band contours in the infrared spectrum of the vapor and the polarization data for the Raman lines quite definitely place 3000, 1446, 1112 and 625 cm.⁻¹ in class A_1 , 1051 cm.⁻¹ in class B_1 and 3080, 943 and 824 cm.⁻¹ in class B_2 . Reasonable assignments of the frequencies 1025 and 1427 cm.⁻¹ which appear in the infrared spectrum are CH_2 wagging in class A_1 and CH_2 scissors in class B_1 , respectively. The Raman frequency of 660 cm.⁻¹ is assigned to the B_1 class, since it is a reasonable value for the C-S stretching frequency of this class and seems too low for any of the A_2 vibrations. This assignment is strengthened by several combination bands which could not be explained if the 660 cm.⁻¹ vibration was placed in the A_2 class.

Normal Coördinate Calculations.—Normal coördinate calculations were carried out for all four symmetry classes of thiacyclopropane. Wilson's¹² GF matrix method was followed, and all of the C-H stretching and CH_2 scissors motions were factored out immediately. The calculations for the A_1 and B_1 classes, in which all of the frequencies not factored out had already been assigned from spectroscopic data, simply showed that these assigned frequencies led to a reasonable and self-consistent set of force constants and thus provided confirmatory evidence for the correctness of the assignment of these frequencies. The calculations for the B_2 and A_2 classes, on the other hand, were used to estimate the values of two unobserved frequencies to use in computing thermodynamic functions. The calculations for these two classes will therefore be presented in some detail.

The coördinates selected to describe the B_2 and A_2 vibrations of the thiacyclopropane molecule were the change of the C-H distance (C-H stretching), Δd ; the change of the angle between the H-C-H and C-C-S planes (CH_2 twisting), $\Delta \psi$; and the change of the angle between the C-C-S plane and the bisector of the H-C-H angle (CH_2 rocking), $\Delta \theta$. The structural parameters used were: C-C distance, 1.53 Å.; C-S distance, 1.82 Å.; C-H distance, 1.09 Å.; and H-C-H angle = H-C-C angle = H-C-S angle, 116° 22'. (When these calculations were made, the more accurate

(11) D. W. Scott, H. L. Finke, M. E. Gross, G. B. Guthrie and H. M. Huffman, *This Journal*, **72**, 2424 (1950).

(12) E. B. Wilson, Jr., *J. Chem. Phys.*, **7**, 1047 (1939); **9**, 76 (1941).

values from microwave studies¹³ were not yet available.) The G matrices were computed numerically and were reduced by factoring out the C-H stretching motions. The potential function used was

$$2V = K_{\psi}[(\Delta\psi_1)^2 + (\Delta\psi_2)^2] + 2L_{\psi}(\Delta\psi_1\Delta\psi_2) + K_{\theta}[(\Delta\theta_1)^2 + (\Delta\theta_2)^2] + 2L_{\theta}(\Delta\theta_1\Delta\theta_2)$$

where the subscripts distinguish the two CH₂ groups. The term $\Delta\psi_1\Delta\psi_2$ has a positive sign when both CH₂ groups twist in the same sense, and the term $\Delta\theta_1\Delta\theta_2$ has a positive sign when both CH₂ groups rock toward the same side of the C-C-S plane. The interaction force constants, $L_{\psi} = 0.170 \times 10^{-11}$ and $L_{\theta} = 0.066 \times 10^{-11}$ ergs radian⁻² were transferred from spiro-pentane,¹⁴ and the observed B₂ frequencies of 824 and 943 cm.⁻¹ were used to evaluate the two principal force constants, $K_{\psi} = 0.920 \times 10^{-11}$ and $K_{\theta} = 1.066 \times 10^{-11}$ ergs radian⁻². With this set of force constants, the two unobserved A₂ frequencies were calculated to be 875 and 1100 cm.⁻¹.

Complete Set of Frequencies.—All of the frequencies of thiacyclopropane have now been discussed except the C-H stretching frequencies in the B₁ and A₂ classes. These certainly have values close to those of their counterparts in the A₁ and B₂ classes and may be given the same values for purposes of thermodynamic calculations.

The complete set of frequencies that was adopted is given in Table III. Appropriate descriptions of the motions are included. For comparison, the

TABLE III

VIBRATIONAL ASSIGNMENTS OF THIACYCLOPROPANE AND RELATED MOLECULES

Thiacyclopropane ^a	Ethylene oxide ^b	Cyclopropane ^c	Spiropentane ^c
C-H stretch			
A ₁ 3000	A ₁ 3000	A ₁ ' 3029	A ₁ & A ₂ 2990
B ₁ 3000 ^d	B ₁ 3000	E' 3024	E 2990
A ₂ 3080 ^d	A ₂ 3060	E'' 3080	A ₂ & B ₁ 3050
B ₂ 3080	B ₂ 3060	A ₂ '' 3103	E 3050
CH ₂ scissors			
A ₁ 1446	A ₁ 1494	A ₁ ' 1504	A ₁ & B ₂ 1500
B ₁ 1427	B ₁ 1469	E' 1432	E 1430
CH ₂ wag			
A ₁ 1025	A ₁ 1120	E' 1028	A ₁ 1033 B ₂ 933
B ₁ 1051	B ₁ 1150	A ₂ ' ..	E 1053
CH ₂ twist			
A ₂ 1100 ^e	A ₂ 1252	E'' ..	A ₂ & B ₁ 1200
B ₂ 943	B ₂ 1172	A ₂ '' ..	E 1157
CH ₂ rock			
A ₂ 875 ^e	A ₂ ~950	E'' 866	A ₂ 872 B ₁ 853
B ₂ 824	B ₂ 820	A ₂ '' 870	E 896
C-C stretch			
A ₁ 1112	A ₁ 1270	A ₁ ' 1189	A ₁ 1150 B ₂ 1397
C-X stretch			
A ₁ 625	A ₁ 874	E' 740	A ₁ 581 B ₂ 870
B ₁ 660	B ₁ 840		E 778

^a This research. ^b Ref. 15. ^c Ref. 16. ^d Used twice. ^e Calcd.

(13) G. L. Cunningham, A. W. Boyd, R. J. Meyers, W. D. Gwinn and W. I. LeVan, *ibid.*, **19**, 676 (1951).

(14) Unpublished calculations, *cf.* ref. 16.

corresponding frequencies of ethylene oxide,¹⁵ cyclopropane¹⁶ and spiro-pentane¹⁶ have been included.

The interpretation of the spectroscopic data in terms of this set of frequencies is given in the fifth column of Table I. Where more than one interpretation is reasonable, the preferred interpretation appears first. All of the observed frequencies have been explained satisfactorily as fundamentals, as overtones and combinations of these observed fundamentals or as frequencies of contaminating polymer with the exception of 866, 1230, 1542?, 1615 and 1949 cm.⁻¹ in the infrared spectrum of the liquid and 892?, 954 and 970 cm.⁻¹ in Thompson and Cave's infrared spectrum of the vapor. Most of these unexplained bands are weak and could well have arisen from traces of impurity in the samples. Only the 1949 cm.⁻¹ band seems too strong to attribute to impurity, and this may well be a combination involving one of the unobserved A₂ fundamentals.

Thermodynamic Functions

Thermodynamic functions were calculated using a harmonic oscillator, rigid rotator model. The moments of inertia, $I_a = 38.18 \times 10^{-40}$, $I_b = 77.50 \times 10^{-40}$ and $I_c = 104.52 \times 10^{-40}$ g. cm.², obtained from microwave studies¹³ were used. The symmetry number is 2. The fundamental constants given by Wagman, *et al.*,¹⁷ were used throughout. Values of the functions $(F_T^0 - H_0^0)/T$, $H_T^0 - H_0^0$, S^0 and C_p^0 at selected temperatures up to 1000°K. are given in Table IV. The values in this table are given to more significant figures than is justified by their absolute accuracy in order to retain the internal consistency of the several thermodynamic functions and also to retain the significance of the increments with temperature of a given function. The calculation of the entropy of liquid thiacyclopropane at 25° from the entropy of the ideal gas is given in Table V.

TABLE IV

THIACYCLOPROPANE: MOLAL THERMODYNAMIC FUNCTIONS

T, °K.	$-(F_T^0 - H_0^0)/T$, cal. deg. ⁻¹	$H_T^0 - H_0^0$, kcal.	S^0 , cal. deg. ⁻¹	C_p^0 , cal. deg. ⁻¹
273.16	51.05	2.424	59.93	11.90
298.16	51.84	2.732	61.01	12.83
300	51.90	2.756	61.09	12.90
400	54.73	4.231	65.31	16.53
500	57.25	6.041	69.33	19.56
600	59.58	8.12	73.12	21.99
700	61.77	10.42	76.66	23.96
800	63.84	12.91	79.98	25.61
900	65.81	15.54	83.08	27.03
1000	67.68	18.30	85.98	28.21

Sunner² has determined the heat of combustion of thiacyclopropane at 20° and has calculated the heat of formation. Similar unpublished, prelimi-

(15) G. L. Cunningham, Thesis, University of California (Berkeley), 1950, through the courtesy of W. D. Gwinn.

(16) D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, M. E. Gross, K. D. Williamson, G. Waddington and H. M. Huffman, *THIS JOURNAL*, **72**, 4664 (1950).

(17) D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **54**, 143 (1945).

TABLE V

MOLAL ENTROPY OF LIQUID THIACYCLOPROPANE, CAL. DEG.⁻¹

Entropy of the ideal gas at 298.16°K. and 1 atm.	61.01
Expansion, $R \ln (760/p)$	2.21
Gas imperfection (estimated)	-0.10
Entropy of real gas at 298.16°K. and 249.7 mm.	63.12
Entropy of condensation, -7240/298.16	-24.28
Entropy of liquid thiacyclopropane at 298.16°K.	38.84

nary measurements and calculations made in this Laboratory by W. N. Hubbard and H. M. Huffman using a different technique¹⁸ are in good agreement with Sunner's results. However, the present understanding of the bomb process in the combustion of sulfur compounds may not be sufficient to eliminate all systematic errors. Sunner's work was taken as the best available and his value, $\Delta H_f = +12.05 \pm 0.15$ kcal./mole,¹⁹ was used for the reaction, $2C(\text{graphite}) + 2H_2(\text{gas}) + S(\text{rhombic}) \rightarrow C_2H_4S(\text{liq.})$. Recalculation of this datum for 25° does not change its value or its precision significantly.²⁰ Adding the value of the heat of vaporization, 7.24 ± 0.05 kcal. mole⁻¹, gives $\Delta H_f = +19.29 \pm 0.16$ kcal. mole⁻¹ for the real gas at saturation pressure; for the ideal gas this becomes $\Delta H_f^0 = +19.33 \pm 0.16$ kcal. mole⁻¹.

The heat, free energy, and equilibrium constant for the formation of thiacyclopropane at selected temperatures were computed using the thermodynamic functions for graphite and hydrogen given by Wagman¹⁷ and for sulfur as given in reference 21. The computed values are given in Table VI.

(18) H. M. Huffman and E. Ellis, *THIS JOURNAL*, **57**, 41 (1935).

(19) Uncertainty assigned by Sunner.

(20) The heat capacity of liquid thiacyclopropane was estimated from the heat capacity of the ideal gas and the difference between the heat capacities of liquid and gaseous ethylene oxide to be 22 cal. deg.⁻¹ mole⁻¹. The change in ΔH_f between 20° and 25° is -0.004 kcal. mole⁻¹.(21) (a) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1949, *et seq.* Series I, Table 14-1 and Series III [S₂(g)]. (b) National Bureau of Standards Report No. 1037.

TABLE VI

MOLAL HEAT, FREE ENERGY AND EQUILIBRIUM CONSTANT FOR THE FORMATION OF THIACYCLOPROPANE

T, °K.	ΔH_f^0 , kcal.	ΔF_f^0 , kcal.	$-\log_{10} K_f$
$2C(\text{graphite}) + 2H_2(g) + S(\text{rhombic}) \rightarrow C_2H_4S(\text{liq.})$			
298.16	12.05	22.16	16.24
$2C(\text{graphite}) + 2H_2(g) + \frac{1}{2}S_2(g) \rightarrow C_2H_4S(g)$			
0	6.82	6.82	∞
298.16	3.93	13.31	9.76
300	3.92	13.37	9.74
400	3.11	16.34	9.09
500	2.48	20.09	8.78
600	1.98	23.66	8.62
700	1.59	27.31	8.53
800	1.31	30.99	8.47
900	1.10	34.72	8.43
1000	0.98	38.46	8.41

In a presentation of the heat, free energy and equilibrium constant for the formation of sulfur compounds at various temperatures, it is inappropriate to use rhombic sulfur as the reference state above 100°. Therefore, this Laboratory has adopted diatomic sulfur, S₂(g), for the reference state in presenting these thermodynamic properties. Although this reference state is unrealistic below 1000°K., the thermodynamic properties of diatomic sulfur have been computed with high accuracy from spectroscopic data,^{21b} using fundamental constants consistent with those adopted by American Petroleum Institute Research Project 44.^{17,22} It is unlikely that the values of the thermodynamic properties of S₂(g) will be changed until a general revision is made of the internally consistent thermodynamic tables of the National Bureau of Standards and the American Petroleum Institute.

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(22) "Selected Values of Properties of Hydrocarbons" by F. D. Rossini, K. S. Pitzer, *et al.*, Circular of the National Bureau of Standards C 461, U. S. Government Printing Office, Washington, D. C., 1947, pp. 8-10.