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[CONTRIBUTION NO. 34 FROM THE THERMODYNAMICS LABORATORY, PETROLEUM EXPERIMENT STATION, BUREAU OF MINES]

Thiacyclobutane: Heat Capacity, Heats of Transition, Fusion and Vaporization, Vapor Pressure, Entropy, Heat of Formation and Thermodynamic Functions[1]

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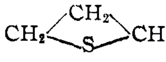
Detailed studies were made of the thermodynamic properties of thiacyclobutane. The properties determined experimentally included: heat capacity of the solid and the liquid between 12 and 321°K., transition temperature (176.7°K.), heat of transition (159.8 cal. mole^{-1}), triple point (199.91°K.), heat of fusion (1971 cal. mole^{-1}), vapor pressure between 48 and 132° [$\log_{10} p = 7.01667 - 1321.331/(t + 224.513)$ (p in mm. and t in °C.)], heat of vaporization (8234 cal. mole^{-1} at 327.53°K.), heat capacity of the vapor ($C^0_p = 20.7$ cal. deg.$^{-1}$ mole^{-1} at 377.20°K.), entropy of the liquid (44.72 and 47.32 cal. deg.$^{-1}$ mole^{-1} at 298.16 and 327.53°K., respectively), entropy of the vapor ($S^0 = 68.17$ and 69.75 cal. deg.$^{-1}$ mole^{-1} at 298.16 and 327.53°K., respectively) and heat of formation [for the reaction: $3C(\text{graphite}) + 3H_2(g) + S(\text{rhombic}) = C_3H_6S(l)$, $\Delta H^0_{298.16} = 6.20$ kcal. mole^{-1}]. The functions $-(F^0 - H^0_0)/T$, $(H^0 - H^0_0)/T$, $H^0 - H^0_0$, S^0 and C^0_p were computed by the methods of statistical mechanics for selected temperatures up to 1000°K. Values of the standard heat, standard free energy and common logarithm of the equilibrium constant of formation were obtained for the same temperatures. Spectroscopic and calorimetric data were shown to favor a planar-ring structure of C_{2v} symmetry for the thiacyclobutane molecule.

The cyclic sulfides constitute one of the classes of organic sulfur compounds that are included in the thermodynamic research program of A.P.I. Research Project 48A. Recent publications from this Laboratory have reported the results of thermodynamic studies of two compounds of this class, the three-membered ring compound, thiacyclopropane[2] and the five-membered ring compound, thiacyclopentane.[3] The present paper reports the results of a thermodynamic study of a third cyclic sulfide, the four-membered ring compound, thiacyclobutane (trimethylene sulfide),



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

[2] G. B. Guthrie, Jr., D. W. Scott and Guy Waddington, THIS JOURNAL, **74**, 2795 (1952).

[3] W. N. Hubbard, H. L. Finke, D. W. Scott, J. P. McCullough, C. Katz, M. E. Gross, J. F. Messerly, R. E. Pennington and G. Waddington, *ibid.*, **74**, 6025 (1952).

A study of the six-membered ring compound, thiacyclohexane, is now in progress in this Laboratory. When this study is complete, it will be possible to compare and correlate the thermodynamic properties of the first four members of the homologous cyclic sulfide series.

The classification of four-membered rings with respect to whether or not they are planar is of current interest in the field of molecular structure. This paper presents evidence in favor of a planar structure for the four-membered ring of the thiacyclobutane molecule.

Units and Auxiliary Data

In the calorimetric studies of this research, measurements of electrical energy, in terms of international joules, were converted to calories by dividing by 4.1833. The ice point (0°C.) was taken to be 273.16°K. The 1951 International Atomic Weights[4] (molecular weight of thiacyclobutane, 74.144) and the values of the fundamental physical constants cited by Wagman, *et al.*,[5] were used for all computations. Values of the thermodynamic properties of carbon (graphite), hydrogen (H_2 gas) and sulfur (rhombic and S_2 gas) were obtained from the compilations of Wagman, *et al.*,[5] and of Evans and Wagman.[6]

Experimental

The experimental work described in the following sections consisted of calorimetric and vapor pressure studies of thiacyclobutane, which yielded values of the heat capacity in the solid, liquid and vapor states, the heats of transition, fusion and vaporization, the vapor pressure, the entropy of the liquid and of the vapor, and the heat of formation.

The Material.—The experimental measurements were made on a sample of thiacyclobutane that was prepared and purified at the Laramie Station of the Bureau of Mines as part of A.P.I. Research Project 48A. Its purity was determined during the low temperature studies by measuring the melting temperature as a function of the fraction melted. The value of the purity so obtained was 99.988 ± 0.006 mole per cent. The purity determination involved the usual assumptions of liquid-soluble, solid-insoluble impurities and ideal solutions. The sample of thiacyclobutane, when it was not being used for experimental measurements, was kept in the dark at a temperature of about 5° to minimize polymerization; immediately before use in each of the experimental studies, it was subjected to bulb-to-bulb distillation to free it from any accumulated polymer.

Low Temperature Studies.—The heat capacity, $C_{sat.}$, of solid and liquid thiacyclobutane was measured between 12 and 321°K., with the results shown in Table I. The measurements were made with an apparatus similar to that described by Ruehrwein and Huffman.[7] The calorimeter was constructed of platinum and equipped with horizontal disks of gold to promote more rapid attainment of thermal equilibrium and to prevent settling of the solid phase during melting studies. The temperature increments used for the measurements (6–10° above 100°K., 5–6° from 50° to 100°K., and less than 10% of the absolute temperature below 50°K.) were small enough that no correction was necessary for non-linear variation of heat capacity with temperature. The heat capacity points, in general, deviated by less than 0.1% from smooth curves on a plot of C_{sat} *vs.* temperature. The accuracy uncertainty of the data probably does not exceed 0.2% except below 30°K., where greater tolerances must be allowed (at most 2% at 12°K.).

TABLE I

MOLAL HEAT CAPACITY OF THIACYCLOBUTANE

T,[a] °K.	C_{sat},[b] cal. deg.$^{-1}$	T,[a] °K.	C_{sat},[b] cal. deg.$^{-1}$	T,[a] °K.	C_{sat},[b] cal. deg.$^{-1}$
Crystals I		58.93	9.684	Crystals II	
12.22	0.445	64.46	10.343	180.20	18.886
12.79	0.523	70.19	10.910	182.43	19.223
13.73	0.656	76.26	11.431	185.13	19.662
14.59	0.790	82.49	11.940	187.99	20.101
15.17	0.883	88.86	12.401	188.70	20.227
16.36	1.097	95.40	12.787	194.15	21.081[c]
16.51	1.125	101.73	13.144	194.70	21.146[c]
18.09	1.441	107.88	13.486		
18.19	1.459	114.22	13.840	Liquid	
19.92	1.829	114.31	13.821	201.98	24.490
20.16	1.892	118.74	14.084	206.44	24.510
21.84	2.283	120.76	14.211	211.32	24.572
22.31	2.397	124.17	14.396	212.09	24.564
24.03	2.820	127.13	14.584	221.33	24.689
24.53	2.942	129.89	14.740	231.25	24.876
26.35	3.402	135.98	15.135	241.08	25.113
26.88	3.531	142.39	15.547	250.81	25.374
28.49	3.935	148.63	16.000	260.43	25.667
29.50	4.193	154.72	16.480	269.93	25.981
32.34	4.902	159.30	16.857	279.31	26.327
35.58	5.652	160.65	17.007	285.16	26.546
39.28	6.456	164.26	17.361	294.37	26.906
43.31	7.253	166.41	17.587	303.46	27.280
47.77	8.052	166.78	17.607	312.44	27.661
52.66	8.828	171.20	18.132	321.29	28.037
53.76	8.978	171.63	18.181		
57.92	9.552				

[a] Mean temperature of the individual measurement. [b] Heat capacity of the condensed phase under its own vapor pressure. [c] Corrected for premelting.

A transition was found to occur in crystalline thiacyclobutane. The following temperatures were observed when different percentages of the sample were transposed from the low temperature form (crystals I) to the high-temperature form (crystals II).

Crystals II, %	46.2	67.4	87.2
Temp., °K.	176.506	176.539	176.706

At the transition, the approach to thermal equilibrium was extremely slow, and a constant temperature was never attained, even when 20 hours were allowed for equilibration after energy input. The temperature in each case appeared to be approaching a limiting value according to an exponential law, and the temperatures listed above are extrapolations of the observed temperatures to the limiting value. The extrapolations amounted to 0.03–0.04°. The value adopted for the transition temperature is 176.7 ± 0.2°K. Triplicate determinations of the molal heat of transition gave the values 159.79, 159.89 and 159.73 cal.

Equilibrium melting temperatures, as a function of the fraction melted, were determined by the method described in an earlier publication.[8] The results are summarized in Table II. The value obtained for the triple point was 199.91°K. The data of Table II were obtained at the beginning of the low temperature studies. To investigate whether or not any polymerization or other contamination of the sample had occurred during the low temperature studies, a similar melting point study was made after all other data had been obtained. The second study gave values for the triple point and purity that did not differ significantly from those obtained the first time.

Triplicate determinations of the molal heat of fusion gave the values 1971.1, 1971.8 and 1971.4 cal. The cryoscopic constant, $\Delta H_{fusion}/RT^2_{T.P.}$, was calculated from the heat of fusion and triple point to be 0.0248 deg.$^{-1}$.

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(7) R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943).

(8) S. S. Todd, G. D. Oliver and H. M. Huffman, *ibid.*, **69**, 1519 (1947).

TABLE II

THIACYCLOBUTANE, MELTING POINT SUMMARY

$T_{T.P.}$ = 199.91°K. Impurity: 0.012 ± 0.006 mole per cent. This value was obtained from the equation $N_2^*/F = 0.0248\ (T_{T.P.} - T_{obsd.})$ where N_2^* is the mole fraction of impurity in the whole sample and F is the fraction of the sample in the liquid state.

Melted, %	$1/F$	T, °K. Obsd.	T, °K. Graph.[b]
9.0	11.1	199.8832	199.8544
24.1	4.15	199.8976	199.8908
49.6	2.016	199.9015[a]	199.9015
68.7	1.456	199.9042	199.9043
87.8	1.139	199.9059[a]	199.9059
100.0	1.000		199.9066
	0		199.9116

[a] A straight line through these points was extrapolated to $1/F = 0$ to obtain the triple point, $T_{T.P.}$. [b] These are the values of T on the straight line referred to in footnote *a*.

The Vapor Pressure.—The vapor pressure of thiacyclobutane was measured from 48 to 132° with the twin ebulliometer system described in an earlier publication from this Laboratory.[9] Water was used as the standard reference substance. The ebulliometer heater was enclosed in a re-entrant well so that the thiacyclobutane came in contact with no surfaces other than glass. The difference between the boiling and condensation temperatures of the sample at 149 mm. was 0.004° at the beginning of the measurements and 0.008° at completion of the measurements. The very small initial difference and the very small change that occurred showed that the sample was practically free of impurity of different volatility and that only an insignificant amount of decomposition and/or polymerization took place during the measurements.

The experimental data are presented in Table III. The "observed" values of the vapor pressure were obtained from the vapor pressure table for water given by Osborne, Stimson and Ginnings.[10] Two equations were selected to represent the vapor pressure of thiacyclobutane, a three constant Antoine equation[11]

TABLE III

THE VAPOR PRESSURE OF THIACYCLOBUTANE

Boiling point °C. Water	Boiling point °C. Thiacyclobutane	Vapor pressure, p(obsd.), mm.	p(obsd.) − p(calcd.), mm. Antoine eq.	p(obsd.) − p(calcd.), mm. Cox eq.
60.000	48.357	149.41	+0.02	0.00
65	54.044	187.57	− .01	− .01
70	59.771	233.72	− .02	− .01
75	65.534	289.13	.00	+ .01
80	71.341	355.22	− .01	.00
85	77.187	433.56	.00	.00
90	83.073	525.86	+ .01	.00
95	88.998	633.99	+ .05	+ .03
100	94.968	760.00	+ .02	.00
105	100.977	906.06	− .01	− .01
110	107.027	1074.6	.0	.0
115	113.118	1268.0	.0	.0
120	119.249	1489.1	.0	.0
125	125.421	1740.8	+ .1	+ .1
130	131.639	2026.0	− .1	− .2

$$\log_{10} p = 7.01667 - 1321.331/(t + 224.513) \quad (1)$$

and a four-constant Cox equation

$$\log_{10} P = A(1 - 368.128/T)$$

where

$$\log_{10} A = 0.802678 - 5.9283 \times 10^{-4}\,T + 5.5834 \times 10^{-7}\,T^2 \quad (2)$$

The units are mm. for p, atm. for P, °C. for t and °K. for T. The simpler Antoine equation is reliable enough for most purposes, but the Cox equation is better for extrapolation outside the range of experimental measurements. The differences between the observed values of the vapor pressure and those calculated by means of the two equations are listed in the last two columns of Table III. The normal boiling point from either equation is 94.97°.

The Heat of Vaporization and Vapor Heat Capacity.—A study of the heat of vaporization and vapor heat capacity of thiacyclobutane was attempted with a cycling vaporizer and flow calorimeter.[12] Because a larger volume of compound was required than in the other kinds of measurements, a second sample of somewhat lower purity (99.9 mole per cent.) was used. The study had to be discontinued when it was found that the sample polymerized quite rapidly under the conditions of the experiments. The following results, which were obtained before polymerization had proceeded to any great extent, are thought to be relatively reliable: heat of vaporization at 327.53°K., 8234 cal. mole^{-1} and vapor heat capacity at 377.20°K. and 190 mm., 20.8 cal. deg.$^{-1}$ mole^{-1}. The heat capacity in the ideal gas state, $C°_p$, was estimated to be 0.1 cal. deg.$^{-1}$ mole^{-1} less than the heat capacity at 190 mm., *i.e.*, 20.7 cal. deg.$^{-1}$ mole^{-1}.

The heat of vaporization at 298.16°K. was calculated from the Clapeyron equation. The temperature coefficient of the vapor pressure was obtained from eq. (2), and the molal volume of the vapor was obtained from the equation of state, $V = RT/P + B$, with B, the second virial coefficient having the value −1.5 l. The foregoing value of the second virial coefficient was estimated from a correlation similar to that described previously,[13] but based on data for sulfur compounds only. The calculated value of the heat of vaporization is 8560 cal. mole^{-1} with an estimated uncertainty of ±50 cal. mole^{-1}.

The Entropy.—The calorimetric and vapor pressure data presented in previous sections were used to compute the entropy of thiacyclobutane for both the liquid and ideal gas states at 298.16 and 327.53°K. Table IV contains a summary of these calculations. For extrapolation of the heat capacity of the solid below 12°K., a Debye function for six degrees of freedom with θ = 152.6° was used.

TABLE IV

THE MOLAL ENTROPY OF THIACYCLOBUTANE, CAL. DEG.$^{-1}$

0–12°K.	Debye extrapolation	0.150	
12–176.7°	Solid, graphical $\int C_{sat.}\, d \ln T$	21.174	
176.7°	Transition, 159.8/176.7	0.904	
176.7–199.91°	Solid, graphical $\int C_{sat.}\, d \ln T$	2.483	
199.91°	Fusion, 1971.4/199.91	9.861	
199.91–298.16°	Liquid, graphical $\int C_{sat.}\, d \ln T$	10.146	
Entropy (±0.10) of liquid at 298.16°K.			44.72
298.16°	Vaporization, 8560/298.16		28.71
298.16°	Gas imperfection (estimated)		0.04
298.16°	Compression, $R \ln (p/760)$		−5.30
Entropy (±0.25) of ideal gas at 298.16°K. and 1 atm.			68.17
298.16–327.53°	Liquid, graphical $\int C_{sat.}\, d \ln T$	2.599	
Entropy (±0.10) of liquid at 327.53°K.			47.32
327.53°	Vaporization, 8234/327.53		25.14
327.53°	Gas imperfection (estimated)		0.05
327.53°	Compression, $R \ln (p/760)$		−2.76
Entropy (±0.25) of ideal gas at 327.53°K. and 1 atm.			69.75

The Heat of Formation.—The heat of formation of thiacyclobutane at 298.16°K. was calculated from a calorimetrically determined value of the heat of combustion. The combustion calorimetry was done with the rotating combustion bomb and associated calorimetric apparatus that have recently been developed in this Laboratory for determination of the heats of combustion of organic sulfur com-

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

(10) N. S. Osborne, H. F. Stimson and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **23**, 261 (1939).

(11) The constants of the Antoine equation were obtained by the least-squares method of C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *ibid.*, **35**, 219 (1945).

(12) G. Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947); G. Waddington and D. R. Douslin, *ibid.*, **69**, 2275 (1947).

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

pounds. A description of the calorimetric apparatus and methods, the detailed heat-of-combustion data for thiacyclobutane, and a comparison with the results of Sunner,[14] who has also determined the heat of formation of this substance, are all included in another publication.[15] Therefore, only the final value for the heat of formation is reported here. This is, for the formation of liquid thiacyclobutane from graphite, gaseous hydrogen and rhombic sulfur, $\Delta H^{\circ}_{298.16} = 6.20 \pm 0.29$ kcal. mole^{-1}. The uncertainty given equals twice the final "over-all" standard deviation.[16]

The heat of vaporization was added to the above value of the heat of formation of the liquid to obtain the heat of formation of the gas. (In the absence of equation-of-state data for thiacyclobutane, the heat of vaporization to the gas in its standard state was estimated to differ from the heat of vaporization to the real gas at saturation pressure by the same amount as in the case of 3-thiapentane,[17] 0.02 kcal. mole^{-1}. This estimate led to a value of 8.58 ± 0.05 kcal. mole for the standard heat of vaporization.) The values of the heat of formation and entropy (of the liquid from Table IV and of the gas from Table VII of a subsequent section) were used to calculate the entropy, free energy and common logarithm of the equilibrium constant of formation. These thermodynamic quantities related to the formation of thiacyclobutane in the liquid and ideal gas states at 298.16°K. are

$$3\text{C(graphite)} + 3\text{H}_2\text{(g)} + \text{S(rhombic)} = \text{C}_3\text{H}_6\text{S(l)}$$

$$\Delta H^0_{298.16} = 6.20 \text{ kcal. mole}^{-1},\ \Delta S^0_{298.16} = -60.62 \text{ cal. deg.}^{-1}\text{ mole}^{-1}$$

$$\Delta F^0_{298.16} = 24.27 \text{ kcal. mole}^{-1},\ \log_{10}K_f = -17.79$$

$$3\text{C(graphite)} + 3\text{H}_2\text{(g)} + \text{S(rhombic)} = \text{C}_3\text{H}_6\text{S(g)}$$

$$\Delta H^0_{298.16} = 14.78 \text{ kcal. mole}^{-1},\ \Delta S^0_{298.16} = -37.20 \text{ cal. deg.}^{-1}\text{ mole}^{-1}$$

$$\Delta F^0_{298.16} = 25.87 \text{ kcal. mole}^{-1},\ \log_{10}K_f = -18.96$$

Thermodynamic Functions

Vibrational Assignment.—The thermodynamic functions $-(F^0 - H^0_0)/T$, $(H^0 - H^0_0)/T$, $H^0 - H^0_0$, S^0 and C^0_p for thiacyclobutane at selected temperatures to 1000°K. were computed by the methods of statistical mechanics. The vibrational assignment used was based on the spectroscopic data of Table V, all of which were obtained by measurements on samples of the same highly purified thiacyclobutane that was used in this research. The sources of these spectroscopic data were: Raman, measurements by E. J. Rosenbaum of the Sun Oil Company[18]; infrared for the liquid, measurements at the Laramie Station of the Bureau of Mines as part of A.P.I. Research Project 48A[19]; infrared for the vapor, measurements by Vernon Thorton of the Phillips Petroleum Company.[20] In the interpretation of the Raman data, it was necessary to recognize the fact that thiacyclobutane polymerizes at an appreciable rate when exposed to ultraviolet light and that some polymerization of the sample is induced by the exciting light when Raman exposures are made. Because of this circumstance, some of the weaker Raman lines listed in Table V are probably those of polymer which accumulated in the sample and not Raman lines of the pure compound.

TABLE V

SPECTRA OF THIACYCLOBUTANE BELOW 1500 CM.$^{-1}$

Abbreviations used: s, strong; m, medium; w, weak; vw, very weak; b, broad; d, diffuse; sh, sharp

Raman	Infrared		
liquid	Liquid	Vapor	Assignment
215 vw			?
245 vw			?
272 vw			?
467 (1)			?
528 (24)			Fundamental A_1
580 (1)			?
609 (3)			$528 + 73 = 601$ B_2
670 (32)*b*	672 s	675 s	Fundamental B_1
698 (16)	701 s	698 s	Fundamental A_1
768 (2)		770 vw	$698 + 73 = 771$ B_2
840 (8)	844 s	844 s	Fundamental B_2
878 (3)			Fundamental A_2
932 (30)		932 m	Fundamental A_1
		958 w	$878 + 73 = 951$ B_1
969 (12)*b,d*	969 s	969 s	Fundamental B_2
991 (5) sh			Fundamental B_1
	ca. 1015 vw		$932 + 73 = 1005$ B_2
1031 vw			?
1042 vw			$969 + 73 = 1042$ A_1
	1055 vw		$2 \times 528 = 1056$ A_1
	1090 vw		?
1137 (1)			Fundamental A_2
1175 (6)	1170 s	1173 s	Fundamental B_1
1205 (3)			$528 + 675 = 1203$ B_1
1217 (3) 1236 (5)	1224 s	1222 s 1236 s	Fundamental A_1 and $528 + 698 = 1226$ A_1
1276 (2)	1271 s	1270 s	Fundamental B_2
1303 vw			Fundamental A_2
1326 (1)			Fundamental B_1
1358 (2) b			$2 \times 675 = 1350$ A_1
		1370 vw	$675 + 698 = 1373$ B_1
1395 (3)			$2 \times 698 = 1396$ A_1
1437 (10)	1441 s	1440 s	Fundamental A_1 & B_1
1464 (9)	*ca.* 1458 m	1460 s	Fundamental A_1

The vibrational assignment will be discussed in terms of a planar-ring structure of the molecule (point group symmetry C_{2v}), since this structure was found to be most consistent with the spectroscopic and calorimetric data. For C_{2v} symmetry, the normal vibrations are divided into symmetry species in the following manner: $8A_1 + 6B_1 + 6B_2 + 4A_2$. The vibrations of species A_1, B_1 and B_2 are active in both spectra; those of species A_2 are Raman-active only. For the values of the moments of inertia given in the next section, the predicted infrared-band contours for the three infrared-active species are: A_1, a triple-minimum contour with a separation of about 21 cm.$^{-1}$ between the P and R branches; B_1, a double-minimum contour with a separation of about 11 cm.$^{-1}$ between the two branches; and B_2, a contour with a strong, sharp Q branch and P and R branches that are weak, broad shoulders on the Q branch.[21]

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(14) S. Sunner, Dissertation, Univ. of Lund, 1949, "Studies on Combustion Calorimetry applied to Organo-Sulfur Compounds," Carl Bloms Boktryckerie, Lund, Sweden, 1949.

(15) W. N. Hubbard, C. Katz and G. Waddington, to be published.

(16) F. D. Rossini and W. E. Deming, *J. Wash. Acad. Sci.*, **29**, 416 (1939).

(17) D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, G. D. Oliver, M. E. Gross, C. Katz, K. D. Williamson, G. Waddington and H. M. Huffman, THIS JOURNAL, **74**, 4656 (1952). 3-Thiapentane was selected because its boiling point is close to that of thiacyclobutane.

(18) American Petroleum Institute Research Project 44 at the Carnegie Institute of Technology, Catalog of Raman Spectral Data, Serial No. 184.

(19) *Ibid.*, Catalog of Infrared Spectral Data, Serial No. 1248.

(20) *Ibid.*, Serial No. 1276.

(21) R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, **6**, 711 (1938).

The predicted contours are illustrated in the upper part of Fig. 1. Thiacyclobutane has two regions of complex infrared absorption where bands overlap, one between 10 and 11μ and the other between 14 and 15μ. These are shown as the solid curves in the lower part of Fig. 1. The dashed curves show schematically the contours of the individual bands which appear to contribute to these regions of complex absorption.

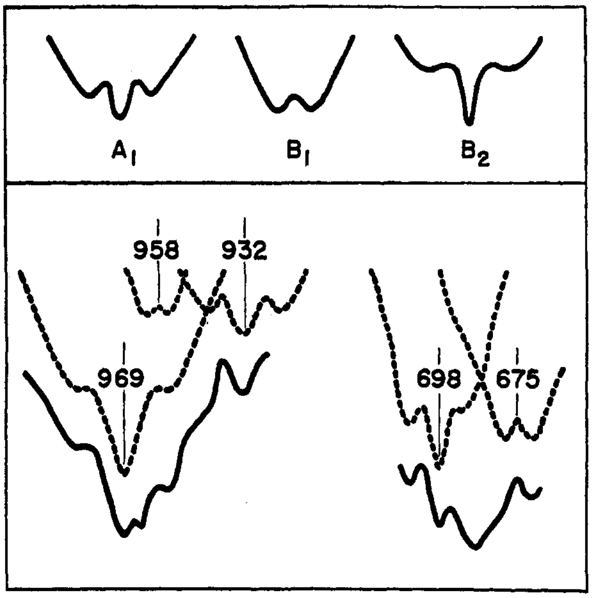

Fig. 1.—Above, predicted contours of the infrared bands of thiacyclobutane; below, regions of complex infrared absorption. Solid lines, observed absorption curve; dashed lines, contours (schematic) of the individual bands contributing to the total absorption.

The assignment of observed frequencies to the individual modes of vibration will now be considered. Two modes are associated with deformations of the four-membered ring, an out-of-plane bending of species B_2 and an in-plane bending of species A_1. These are the only modes that are expected to have frequencies below 600 cm.$^{-1}$. The frequency of the former could not be assigned directly from the observed spectra, but that of the latter could be assigned from the Raman line at 528 cm.$^{-1}$, which has the high intensity expected of a totally symmetric fundamental. The two C–S stretching frequencies appear strongly in both spectra at 675 and 698 cm.$^{-1}$. The band contours in the infrared spectrum of the vapor showed the 675 cm.$^{-1}$ frequency to be that of a B_1 vibration and the 698 cm.$^{-1}$ frequency to be that of an A_1 vibration. There are three CH_2 rocking modes, two of species B_2 and one of species A_2. The 844 and 969 cm.$^{-1}$ frequencies, the infrared bands of which have B_2 contours, and the 878 cm.$^{-1}$ frequency, which is the only one in the expected range that appears only in the Raman effect, were assigned to these CH_2 rocking modes. The two C–C stretching modes would be expected to appear with at least moderate intensity in the Raman spectrum. The previously unassigned Raman lines at 932 and 991 cm.$^{-1}$ were assigned to these modes. The 932 cm.$^{-1}$ frequency also appears in the infrared spectrum with an A_1 band contour; the symmetry species are thus 932 cm.$^{-1}$, A_1 and 991 cm.$^{-1}$, B_1. Of the three CH_2 wagging modes, one is of species A_1 and two of species B_1. The fundamental at about 1226 cm.$^{-1}$, the resonance interaction of which with the sum-combination 528 + 698 = 1226(A_1) gives rise to the observed doublet, 1222–1236 cm.$^{-1}$, was assigned to the A_1 mode. The 1173 cm.$^{-1}$ frequency, the band contour of which in the infrared spectrum is suggestive of a poorly resolved B_1 band, was assigned to one of the B_1 modes. No frequency could be assigned directly from the selection rules to the second B_1 mode. There are three CH_2 twisting modes, one of species B_2 and two of species A_2. The 1272 cm.$^{-1}$ frequency, the band contour of which in the infrared spectrum is suggestive of a poorly resolved B_2 band, was assigned to the B_2 mode. No frequencies could be assigned directly to either of the A_2 modes. The three CH_2 bending (scissors) modes, two of species A_1 and one of species B_1, are expected to have frequencies in the range 1400–1500 cm.$^{-1}$. The observed frequencies of 1440 and 1460 cm.$^{-1}$ were assigned to the A_1 modes, and the former was also assigned to the B_1 mode, the frequency of which is probably not resolved from that of its A_1 counterpart. The six C–H stretching frequencies are not completely resolved in the observed spectra. Since these frequencies are relatively unimportant from a thermodynamic standpoint, no attempt was made to assign them in detail, and an average value of 2950 cm.$^{-1}$ was adopted for all six frequencies.

Four modes then remained unassigned: ring deformation, B_2; CH_2 wagging, B_1; and two CH_2 twisting modes, A_2. The last three were expected to have frequencies in the range 1100–1400 cm.$^{-1}$. Six Raman lines and one infrared band in this range were as yet unassigned; however, four of these seven observed frequencies were readily explained as overtones or combinations. The remaining three (1137, 1303 and 1326 cm.) were selected as the fundamental frequencies. Their assignment to particular symmetry species was rather arbitrary. The B_2 ring deformation frequency must have a value of approximately 73 cm.$^{-1}$ in order to fit the calorimetric values of the entropy. A frequency as low as this could readily escape detection in the Raman effect by being obscured by Rayleigh scattering from the exciting frequency. A number of observed frequencies could be explained as sum-combinations of observed fundamentals with an unobserved fundamental near 73 cm.$^{-1}$, notably the infrared band at 958 cm.$^{-1}$, the Raman line and infrared band at 770 cm.$^{-1}$, and the Raman line at 609 cm.$^{-1}$ (which seems slightly too intense to attribute to polymeric impurity). The infrared bands at 958 and 770 cm.$^{-1}$ have contours consistent with their interpretation as sum-combinations with a 73 cm.$^{-1}$ frequency of species B_2.

Thus far the point group symmetry of the molecule has been assumed to be C_{2v} (symmetry number = 2). If the molecule has lower symmetry (effective symmetry number = 1), then the value of the B_2 ring deformation frequency that is required to fit the calorimetric values of the entropy is 148 cm.$^{-1}$ instead of 73 cm.$^{-1}$. A value of 148 cm.$^{-1}$ leaves unexplained those observed frequencies that are easily explained as sum-combinations if the value is 73 cm.$^{-1}$. The spectroscopic and calorimetric data thus favor the structure of C_{2v} point group symmetry.

The complete set of vibrational frequencies that was used for the calculation of the thermodynamic functions is given in Table VI. With this assignment, only seven of the observed frequencies in Table V remain unexplained: the very weakest infrared band of the liquid and six Raman lines whose intensity on the scale of Table V is 1 or less. It is likely that most of these unexplained Raman lines are to be attributed to polymer which formed in the sample during the Raman exposures.

TABLE VI

VIBRATIONAL FREQUENCIES USED FOR THERMODYNAMIC CALCULATIONS, CM.$^{-1}$

	A_1	B_1	A_2	B_2
Ring deformation	528			73
C–S stretching	698	675		
CH_2 rocking			878	844 & 969
C–C stretching	932	991		
CH_2 wagging	1226	1173 & 1326		
CH_2 twisting			1137 & 1303	1272
CH_2 bending	1440 & 1460	1440		
C–H stretching	2950 (2)	2950	2950	2950 (2)

Moments of Inertia.—The moments of inertia of the thiacyclobutane molecule were calculated for a structure with C_{2v} point group symmetry, with normal bond distances, and with ring angles that were estimated by an approximate calculation to be the values that would minimize the strain energy. These bond distances and angles are: C–S distance, 1.82 Å.; C–C distance 1.54 Å.; C–H distance, 1.09 Å.; C–S–C angle, 79°; H–C–H angle, H–C–C angles and H–C–S angles equal for the α-methylene groups; and H–C–H angle and H–C–C angles equal for the β-methylene group. The principal moments of inertia for this structure are 0.824, 1.234 and 1.893 × 10^{-38} g. cm.^{2}, and their product is 1.925 × 10^{-114} g.^{3} cm.^{6}.

Thermodynamic Functions.—The vibrational assignment and moment-of-inertia values of the two previous sections were used to compute the functions $-(F^0 - H_0^0)/T$, $(H^0 - H_0^0)/T$, $H^0 - H_0^0$, S^0 and C_p^0 at selected temperatures up to 1000°K. The computed functions are given in columns 2–6 of Table VII. The consistency of these functions with the calorimetric results may be judged by the following comparison of calculated and observed values

	T, °K.	Calcd., cal. deg.$^{-1}$ mole^{-1}	Obsd., cal. deg.$^{-1}$ mole^{-1}
S^0	298.16	68.14	68.17
S^0	327.53	69.76	69.75
C^0_p	377.20	20.74	20.7

The calorimetric value of the heat of formation at 298.16°K. was used with the computed functions to obtain values of the standard heat of formation, standard free energy of formation, and common logarithm of the equilibrium constant of formation for selected temperatures up to 1000°K. These are given in columns 7–9 of Table VII. The reference state for elemental sulfur is diatomic sulfur gas, S_2(g). Some entries in Table VII are given to more decimal places than are justified by their absolute accuracy to retain internal consistency throughout the table.

TABLE VII

MOLAL THERMODYNAMIC PROPERTIES OF THIACYCLOBUTANE

T, °K.	$-(F^0 - H_0^0)/T$, cal. deg.$^{-1}$	$(H^0 - H_0^0)/T$, cal. deg.$^{-1}$	$H^0 - H_0^0$ kcal.	S^0, cal. deg.$^{-1}$	C_p^0 cal. deg.$^{-1}$	ΔH_f^{0a} kcal.	ΔF_f^{0a} kcal.	$\log_{10} Kf^a$
0	0	0	0	0	0	3.91	3.91	$-\infty$
273.16	55.86	10.87	2.970	66.73	15.31	−0.26	14.94	−11.95
298.16	56.85	11.29	3.367	68.14	16.57	−0.62	16.32	−11.96
300	56.92	11.33	3.398	68.24	16.66	−0.65	16.43	−11.97
400	60.44	13.32	5.327	73.76	21.89	−1.94	22.32	−12.20
500	63.64	15.51	7.756	79.16	26.56	−2.98	28.51	−12.46
600	66.67	17.69	10.61	84.35	30.45	−3.77	34.89	−12.71
700	69.55	19.75	13.83	89.30	33.69	−4.37	41.39	−12.92
800	72.31	21.67	17.33	93.98	36.40	−4.80	47.95	−13.10
900	74.97	23.43	21.09	98.40	38.70	−5.07	54.56	−13.25
1000	77.52	25.06	25.06	102.59	40.67	−5.21	61.20	−13.27

[a] The standard heat, standard free energy and common logarithm of the equilibrium constant for the formation of thiacyclobutane by the reaction: $3C(\text{graphite}) + 3H_2(g) + {}^1/_2S_2(g) = C_3H_6S(g)$.

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