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1-Butanethiol and 2-Thiapentane. Experimental Thermodynamic Studies between 12 and 500°K.; Thermodynamic Functions by a Refined Method of Increments[1]

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From experimental thermodynamic studies of 1-butanethiol and 2-thiapentane, values of the standard entropy, heat capacity and heat of formation of both substances in the vapor state were obtained. Thermodynamic functions between 0 and 1000°K. were computed by a refined method of increments. The method included application of empirical corrections based on the experimental values of entropy and heat capacity. Values of the heat, free energy and logarithm of the equilibrium constant of formation between 0 and 1000°K. also were computed. The experimental studies provided the following information for each substance: Values of the heat capacity for the solid (12°K. to the triple point), the liquid (triple point to 325°K.) and the vapor (360 to 500°K.); the triple point temperature; the heat of fusion; the entropy of the liquid at 298.16°K.; the heat of vaporization for pressures between 1/4 and 1 atm.; the second virial coefficient, B, in the equation of state, $PV = RT(1 + B/V)$; the vapor pressure (for 1-butanethiol only); and the standard heat of formation.

Comprehensive thermodynamic studies of all seven isomeric $C_4H_{10}S$ thiols and sulfides are included in the program of American Petroleum Institute Research Project 48A in this Laboratory. Results for 3-thiapentane,[2] 2-methyl-2-propanethiol[3] and 3-methyl-2-thiabutane[4] have already been published. For these three isomers, thermodynamic functions were calculated by detailed methods of statistical mechanics. For two other isomers, 2-butanethiol and 2-methyl-1-propanethiol, similar detailed calculations have been undertaken in this Laboratory. For the two remaining isomers that are the subject of this paper, 1-butanethiol (*n*-butyl mercaptan) and 2-thiapentane (methyl *n*-propyl sulfide), accurate calorimetric data were obtained, but it was not feasible to make detailed calculations of thermodynamic functions by the methods of statistical mechanics. In particular, it was not practical either to assign observed vibrational frequencies to each of the several individual rotational tautomers or to use calorimetric data to determine the shape of the two different unsymmetrical barriers to internal rotation of each molecule. Therefore, a simple empirical refinement of the usual method of increments was used instead of the methods of statistical mechanics. This refined method of increments yielded values of the thermodynamic functions of 1-butanethiol and 2-thiapentane almost as reliable as those obtained by detailed calculations for the other isomers.

The experimental part of this investigation consisted of studies by low temperature calorimetry, flow calorimetry, comparative ebulliometry and combustion calorimetry. The detailed results are given later in the Experimental section. However, the more pertinent results that are needed for the calculation of thermodynamic properties, as discussed in the next section, are collected in Table I.

TABLE I

OBSERVED AND CALCULATED THERMODYNAMIC PROPERTIES FOR THE VAPOR STATE

	Entropy, $S°$, cal. deg.$^{-1}$ mole^{-1}			Heat capacity, $C_p°$, cal. deg.$^{-1}$ mole^{-1}	
T, °K.	Obsd.	Calcd.	T, °K.	Obsd.	Calcd.
		1-Butanethiol			
330.62	92.71	92.70	360.20	32.35	32.37
349.70	94.41	94.44	382.20	33.82	33.80
371.62	96.30	96.42	417.20	36.08	36.04
			453.20	38.29	38.28
			500.20	41.03	41.08

$4C(\text{graphite}) + 5H_2(g) + {}^1/_2S_2(g) = C_4H_{10}S(g)$

$\Delta Hf°_{298.16}(\text{obsd.}) = -36.29 \pm 0.30$ kcal. mole^{-1}

		2-Thiapentane			
328.12	91.62	91.61	375.20	33.05	33.07
347.02	93.32	93.32	400.20	34.63	34.65
368.70	95.23	95.26	433.20	36.72	36.69
			466.20	38.66	38.67
			500.20	40.63	40.62

$4C(\text{graphite}) + 5H_2(g) + {}^1/_2S_2(g) = C_4H_{10}S(g)$

$\Delta Hf°_{298.16}(\text{obsd.}) = -34.78 \pm 0.24$ kcal. mole^{-1}

Calculation of Thermodynamic Properties

The Refined Method of Increments.—When an *n*-alkyl group in the molecule of a compound is lengthened by $-CH_2-$, the change in any thermodynamic property, after allowing for any change in symmetry, is called a CH_2 increment. The CH_2 increments are approximately independent of the length of the alkyl group and of the nature of the other part of the molecule. In the ordinary method of increments, the thermodynamic functions of a substance are estimated by addition of CH_2 increments to known thermodynamic functions of a lower homolog, with provision for any difference in symmetry.

Values of the thermodynamic functions are known for the next lower homologs of both 1-butanethiol and 2-thiapentane, namely, 1-propanethiol[5] and 2-thiabutane.[6] Values to use for

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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 Measurement of their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.

(2) D. W. Scott, H. L. Finke, W. N. Hubbard, J. P. McCullough, G. D. Oliver, M. E. Gross, C. Katz, K. D. Williamson, Guy Waddington and H. M. Huffman, THIS JOURNAL, **74**, 4656 (1952).

(3) J. P. McCullough, D. W. Scott, H. L. Finke, W. N. Hubbard, M. E. Gross, C. Katz, R. E. Pennington, J. F. Messerly and Guy Waddington, *ibid.*, **75**, 1818 (1953).

(4) J. P. McCullough, H. L. Finke, J. F. Messerly, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, *ibid.*, **77**, 6119 (1955).

(5) R. E. Pennington, D. W. Scott, H. L. Finke, J. P. McCullough, J. F. Messerly, I. A. Hossenlopp and Guy Waddington, *ibid.*, **78**, 3266 (1956).

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the CH_2 increments could have been obtained from any of various pairs of homologs. However, for the present instance of *n*-alkyl groups attached to sulfur atoms, it seemed most appropriate to use the differences in the known thermodynamic functions of 1-propanethiol[5] and ethanethiol.[7]

Values of the heat capacity, $C_p°$, calculated by the ordinary method of increments with CH_2 increments so obtained, differed significantly from the experimental values. However, for both 1-butanethiol and 2-thiapentane, the difference was essentially constant over the entire temperature range of the experimental measurements. The ordinary method of increments was therefore refined by inclusion of a constant term, a, in the calculated values of heat capacity between 273.16 and 1000°K. Terms obtained by appropriate integration of the constant heat capacity term were included in the other thermodynamic functions over the same temperature range. The complete expressions used for the thermodynamic functions are

$$C_p° \begin{array}{c}\text{(1-butanethiol} \\ \text{or} \\ \text{2-thiapentane)}\end{array} = C_p° \begin{array}{c}\text{(1-propanethiol} \\ \text{or} \\ \text{2-thiabutane)}\end{array} + C_p°\ \text{(1-propanethiol)} - C_p°\ \text{(ethanethiol)} + a$$

$$S° \begin{array}{c}\text{(1-butanethiol} \\ \text{or} \\ \text{2-thiapentane)}\end{array} = S° \begin{array}{c}\text{(1-propanethiol} \\ \text{or} \\ \text{2-thiabutane)}\end{array} + S°\text{(1-propanethiol)} - S°\ \text{(ethanethiol)} + a \ln T + b$$

$$(H° - H°_0) \begin{array}{c}\text{(1-butanethiol} \\ \text{or} \\ \text{2-thiapentane)}\end{array} = (H° - H°_0) \begin{array}{c}\text{(1-propanethiol} \\ \text{or} \\ \text{2-thiabutane)}\end{array} + (H° - H°_0)\text{(1-propanethiol)} - (H° - H°_0)\text{(ethanethiol)} + aT$$

Strictly, the expression for $H° - H°_0$ should include an integration constant, which has a nonzero value because the correction term to the heat capacity must decrease to zero at 0°K. and not retain the constant value a over the whole range 273.16°K. down to 0°K. Since this integration constant cannot be evaluated from the calorimetric data and since it cancels out in any practical calculation of the heat or free energy of a chemical reaction, except for temperatures below 273.16°K., it has been omitted. Values of a were selected to give satisfactory agreement with the experimental values of heat capacity. Values of b were then selected to give agreement with the experimental values of entropy. The values used for a and b are tabulated below.

Substance	a, cal. deg.$^{-1}$ mole^{-1}	b, cal. deg.$^{-1}$ mole^{-1}
1-Butanethiol	0.31	−2.12
2-Thiapentane	0.05	−0.67

The smaller values of a and b for 2-thiapentane reflect the fact that the CH_2 increments used are strictly for replacement of an ethyl group attached to sulfur with an *n*-propyl group, as in the change of 2-thiabutane to 2-thiapentane but not in the change of 1-propanethiol to 1-butanethiol.

Values of thermodynamic functions calculated by the refined method of increments are listed in columns 2–6 of Tables II and III. Calculated values of the entropy and heat capacity are compared with the observed values in Table I. It was possible to adjust the calculated values to fit the entropy and heat capacity exactly at only a single temperature each. However, for both substances, satisfactory agreement was obtained at all temperatures for which there were experimental observations.

The excellent agreement obtained with the refined method of increments illustrates the utility of vapor heat capacity data even for substances too complex to treat by the detailed methods of statistical mechanics.

The Heat, Free Energy and Equilibrium Constant of Formation.—The values of the thermodynamic functions, the experimental values of $\Delta Hf°_{298.16}$ given in Table I and values of the thermodynamic functions of C(graphite),[8] H_2(g)[8] and S_2(g)[9] were used to compute values of $\Delta Hf°$, $\Delta Ff°$ and $\log_{10} Kf$ at selected temperatures from 0 to 1000°K. The computed values are listed in columns 7–9 of Tables II and III. The uncertainty in the values of $\Delta Hf°$ and $\Delta Ff°$ is somewhat greater at 0°K. than at the other temperatures listed because the integration constant was not included in the expression for $H° - H°_0$.

TABLE II

THE MOLAL THERMODYNAMIC PROPERTIES OF 1-BUTANETHIOL[a]

T, °K.	$(F° - H°_0)/T$, cal. deg.$^{-1}$	$(H° - H°_0)/T$, cal. deg.$^{-1}$	$H° - H°_0$, kcal.	$S°$, cal. deg.$^{-1}$	$Cp°$, cal. deg.$^{-1}$	$\Delta Hf°$,[b] kcal.	$\Delta Ff°$,[b] kcal.	$\log_{10} Kf$[b]
0	0	0	0	0	0	−29.84	−29.84	Infinite
273.16	−68.75	18.52	5.060	87.27	26.63	−35.82	−9.20	7.36
298.16	−70.42	19.26	5.741	89.68	28.24	−36.29	−6.75	4.95
300	−70.52	19.33	5.799	89.85	28.37	−36.32	−6.56	4.78
400	−76.49	22.43	8.972	98.92	34.95	−38.01	3.62	−1.98
500	−81.84	25.55	12.78	107.39	41.07	−39.38	14.19	−6.20
600	−86.76	28.60	17.16	115.36	46.54	−40.43	25.02	−9.11
700	−91.39	31.52	22.07	122.91	51.37	−41.16	35.99	−11.24
800	−95.79	34.25	27.40	130.04	55.68	−41.63	47.03	−12.85
900	−100.02	36.85	33.17	136.87	59.54	−41.81	58.09	−14.11
1000	−103.98	39.31	39.31	143.29	62.95	−41.71	69.24	−15.13

[a] To retain internal consistency, some values in this table are given to one more decimal place than is justified by the absolute accuracy. [b] The standard heat, standard free energy and common logarithm of the equilibrium constant of formation by the reaction: $4C(\text{graphite}) + 5H_2(g) + {}^1/_2S_2(g) = C_4H_{10}S(g)$.

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[7] J. P. McCullough, W. N. Hubbard, F. R. Frow, I. A. Hossenlopp and Guy Waddington, THIS JOURNAL, **79**, 561 (1957).

[8] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **34**, 143 (1945).

[9] W. H. Evans and D. D. Wagman, *ibid.*, **49**, 141 (1952).

TABLE III

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-THIAPENTANE[a]

T, °K.	$(F^\circ - H^\circ_0)/T$, cal. deg.$^{-1}$	$(H^\circ - H^\circ_0)/T$, cal. deg.$^{-1}$	$H^\circ - H^\circ_0$, kcal.	S°, cal. deg.$^{-1}$	Cp°, cal. deg.$^{-1}$	ΔHf°,[b] kcal.	ΔFf°,[b] kcal.	$\log_{10} Kf$[b]
0	0	0	0	0	0	−28.20	−28.20	Infinite
273.16	−68.40	18.05	4.931	86.45	26.45	−34.31	−7.46	5.97
298.16	−70.02	18.82	5.611	88.84	28.05	−34.78	−4.99	3.66
300	−70.13	18.89	5.666	89.02	28.17	−34.81	−4.80	3.50
400	−75.98	22.02	8.808	98.00	34.64	−36.53	5.47	−2.99
500	−81.23	25.16	12.58	106.39	40.61	−37.94	16.14	−7.05
600	−86.10	28.16	16.90	114.26	45.86	−39.05	27.05	−9.85
700	−90.66	31.03	21.72	121.69	50.43	−39.86	38.14	−11.91
800	−94.98	33.69	26.95	128.67	54.45	−40.44	49.32	−13.47
900	−99.13	36.20	32.58	135.33	58.02	−40.75	60.53	−14.70
1000	−103.03	38.56	38.56	141.59	61.14	−40.82	71.83	−15.70

[a,b] See footnotes of Table II.

Experimental

The 1951 International Atomic Weights[10] and the 1951 values of the fundamental physical constants[11] were used. The reported values are based on a molecular weight of 90.186 for $C_4H_{10}S$ and the following relations: 0° = 273.16°K. and 1 cal. = 4.1840 abs. j. = 4.1833 int. j. Measurements of temperature were made with platinum resistance thermometers calibrated in terms of the International Temperature Scale[12] between 90 and 500°K. and the provisional scale[13] of the National Bureau of Standards between 11 and 90°K. Measurements of mass, energy and resistance were made in terms of standard devices calibrated at the National Bureau of Standards.

The Materials.—The materials used for low temperature calorimetry, comparative ebulliometry and combustion calorimetry were portions of standard samples of sulfur compounds prepared at the Laramie, Wyoming, station of the Bureau of Mines. The standard sample numbers are API-USBM 14 for 1-butanethiol and API-USBM 18 for 2-thiapentane. In calorimetric melting point studies to be discussed later, the purity of these standard samples was found to be 99.990 ± 0.005 mole % for 1-butanethiol and 99.980 ± 0.005 mole % for 2-thiapentane. For flow calorimetry, which required a larger volume of material, samples of somewhat lower purity were provided by the Laramie station. The reported purity of these samples was 99.8 mole % for 1-butanethiol and 99.85 mole % for 2-thiapentane. The samples were received in sealed ampoules with internal break-off tips. Precautions in handling and use included storage in the dark in a refrigerated room, transferring by vacuum distillation in closed systems, allowing a minimum of contact with air and gases other than helium and, when necessary, drying with suitable effective drying agents before use in experimental measurements.

The Heat Capacity in the Solid and Liquid States.—Low temperature thermal studies were made in an adiabatic calorimetric system similar to that described in previous publications.[14] The platinum calorimeter with internal heat-distributing disks of gold contained about half a mole of sample. Helium (40–80 mm. pressure at room temperature) was sealed in the calorimeter with the sample to promote thermal equilibration at low temperatures.

The observed values of the heat capacity at saturation pressure C_{satd}, are listed in Table IV. Values immediately below the melting points have not been corrected for the effects of premelting caused by impurities. The temperature increments used in the measurements (about 10% of the absolute temperature below 50°K. and 5 to 11° above 50°K.) were small enough that corrections for non-linear variation of heat capacity with temperature were unnecessary. Above 30°K., the accuracy uncertainty of the heat capacity data probably does not exceed 0.2%; below 30°K., the accuracy uncertainty is greater. The heat capacity of the liquids may be represented by the following empirical equations. The units are C_{satd} in cal. deg.$^{-1}$ mole^{-1} and T in °K.

1-Butanethiol:

$$C_{\text{satd}} = 58.181 - 0.22480\,T + 7.7232 \times 10^{-4}T^2 - 7.0400 \times 10^{-7}T^3 \quad (1)$$

2-Thiapentane

$$C_{\text{satd}} = 52.841 - 0.18648\,T + 6.9375 \times 10^{-4}T^2 - 6.7448 \times 10^{-7}T^3 \quad (2)$$

These equations fit the observed values with average deviations of 0.03% for 1-butanethiol (160 to 314°K.) and 0.01% for 2-thiapentane (200 to 315°K.).

The Heat of Fusion, Triple Point, Cryoscopic Constants and Purity of Sample.—Two determinations were made of the heat of fusion of each compound. Measurements were made of the enthalpy change over a finite temperature interval that included the triple point. Subtraction of the energy absorbed non-isothermally by the crystals and liquid gave the heat of fusion. Corrections for the effects of premelting were applied. The results are

1-Butanethiol, ΔH_{fusion}:
2499.1, 2500.2; accepted 2500 cal. mole^{-1}

2-Thiapentane, ΔH_{fusion}:
2369.2, 2369.3; accepted 2369 cal. mole^{-1}

Studies of the equilibrium melting temperature, T_{obsd}, as a function of fraction of total sample melted, F, were made by the procedure outlined in an earlier publication.[15] The results are summarized in Table V. The values of T_{obsd} were plotted as a function of $1/F$, and the triple point temperature, $T_{\text{T.P.}}$, was obtained by linear extrapolation to zero value of $1/F$. If the impurities present form ideal solutions in the liquid phase and are insoluble in the solid phase, the relation between mole fraction of total impurity, N_2^*, and the melting point depression, $\Delta T = T_{\text{T.P.}} - T_{\text{obsd}}$, is[16]

$$-\ln(1 - N_2) = A\Delta T(1 + B\Delta T + \ldots\ldots..) \quad (3)$$

where $N_2 = N_2^*/F$. For each compound, the first cryoscopic constant, $A = \Delta H_{\text{fusion}}/RT^2_{\text{T.P.}}$, and the second cryoscopic constant, $B = 1/T_{\text{T.P.}} - \Delta C_{\text{fusion}}/2\Delta H_{\text{fusion}}$, were calculated from the observed values of $T_{\text{T.P.}}$, ΔH_{fusion} and ΔC_{fusion}. Application of eq. 3 in its simplified form (for $N_2^* << 1$), $N_2^* = AF\Delta T$, yielded values of the concentration of impurity in each sample.

The Thermodynamic Properties in the Solid and Liquid States.—Values of the free energy function, heat content function, heat content, entropy and heat capacity at selected temperatures were computed from the low temperature calorimetric data for each substance. The values at

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(11) F. D. Rossini, F. T. Gucker, Jr., H. L. Johnston, L. Pauling and G. W. Vinal, *ibid.*, **74**, 2699 (1952).

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(14) R. A. Ruehrwein and H. M. Huffman, THIS JOURNAL, **65**, 1620 (1943); H. M. Huffman, S. S. Todd and G. D. Oliver, *ibid.*, **71**, 584 (1949); D. W. Scott, D. R. Douslin, M. E. Gross, G. D. Oliver and H. M. Huffman, *ibid.*, **74**, 883 (1952).

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TABLE IV

THE MOLAL HEAT CAPACITY IN CAL. DEG.$^{-1}$

T, °K.[a]	C_{satd}[b]	T, °K.[a]	C_{satd}[b]	T, °K.[a]	C_{satd}[b]
1-Butanethiol					
Crystals		50.80	9.969	150.23	23.751[c]
12.91	0.802	55.07	10.814	Liquid	
13.08	.839	56.19	11.037	160.23	39.09
14.21	1.059	59.19	11.602	166.53	38.90
14.67	1.154	63.87	12.467	171.28	38.78
15.63	1.347	69.01	13.319	174.27	38.74
16.34	1.511	74.57	14.216	177.08	38.70
17.21	1.715	80.36	15.090	182.00	38.61
18.14	1.940	85.30	15.818	190.69	38.53
18.95	2.140	86.04	15.942	200.33	38.49
20.27	2.481	90.29	16.511	209.93	38.52
20.91	2.645	91.87	16.732	219.97	38.60
22.61	3.093	96.37	17.275	230.44	38.76
23.13	3.237	97.89	17.475	233.63	38.84
25.03	3 758	103.04	18.095	243.13	39.07
25.46	3.872	109.50	18.872[c]	253.60	39 37
27.61	4.454	116.30	19.667[c]	263.98	39.71
27.84	4.516	123.84	20.531[c]	274.26	40.10
30.51	5.237	131.59	21.425[c]	284.44	40.56
33.66	6.066	135.94	21.916[c]	294.51	41.01
37.26	6.944	138.97	22.283[c]	304.48	41.47
41.38	7.919	143.21	22.803[c]	314.33	41.95
45.86	8.912	146.02	23.155[c]		
2-Thiapentane					
Crystals		50.70	10.257	150.37	24.070[c]
12.57	0.837	55.00	11.186	Liquid	
12.87	.893	56.02	11.395	167.45	37.75
13.86	1.096	59.92	12.194	170.80	37.76
14.54	1.232	65.25	13.230	172.90	37.75
15.27	1.390	70.58	14.153	176.79	37.76
16.47	1.670	75.93	15.037	180.79	37.76
16.83	1.749	81.51	15.934	190.63	37.81
18.55	2.151	86.41	16.673	200.89	37.91
18.57	2.161	87.44	16.839	211.58	38.03
20.43	2.626	91.71	17.415	222.19	38.26
20.68	2.686	97.22	18.109	227.42	38.38
22.64	3.190	103.38	18.875	237.90	38.67
22.95	3.273	106.13	19.187	248.28	38.98
25.05	3.829	109.77	19.621	258.56	39.34
25.31	3.897	112.43	19.920[c]	268.75	39.73
27.51	4.490	115.93	20.322[c]	278.82	40.16
27.85	4.579	122.38	21.027[c]	288.79	40.60
30.72	5.361	129.12	21.754[c]	298.66	41.05
33.86	6.192	136.11	22.481[c]	304.94	41.36
37.44	7.095	139.07	22.778[c]	308.85	41.55
41.53	8.115	143.35	23.239[c]	315.43	41.88
45.89	9.159	147.92	23.773[c]	325.78	42.42

[a] T is the mean temperature of each heat capacity measurement. [b] C_{satd} is the heat capacity of the condensed phase under its own vapor pressure. [c] Not corrected for the effects of premelting caused by impurities.

10°K. were calculated from Debye functions with the following parameters: for 1-butanethiol, 5 degrees of freedom, $\theta = 125.8°$; for 2-thiapentane, 4.5 degrees of freedom, $\theta = 116.5°$. These parameters were evaluated from the heat capacity data between 12 and 20°K. The thermodynamic properties above 10°K. were computed by numerical integration of values of C_{satd} read from large scale plots of the data of Table IV and use of the observed values of ΔH_{fusion} and $T_{T.P.}$ The results are given in Table VI. Corrections for the effects of premelting have been applied to the "smoothed" data recorded in Table VI.

TABLE V

MELTING POINT STUDIES

1-Butanethiol

Triple point temperature, $T_{T.P.}$ = 157.47 ± 0.05°K.; first cryoscopic constant, A = 0.05073 deg.$^{-1}$; second cryoscopic constant, B = 0.00341 deg.$^{-1}$; concentration of impurity = 0.010 ± 0.005 mole %.

Melted, %	1/F	T, °K. Obsd.	Graph.[a]
10.69	9.35	157.4496	157.4496
25.57	3.911	157.4612	157.4599
49.62	2.015	157.4635	157.4635
69.97	1.429	157.4652	157.4646
88.47	1.130	157.4652	157.4652
100.00	1.000		157.4654
Pure	0.000		157.4673

2-Thiapentane

Triple point temperature, $T_{T.P.}$ = 160.17 ± 0.05°K.; first cryoscopic constant, A = 0.04647 deg.$^{-1}$; second cryoscopic constant, B = 0.00355 deg.$^{-1}$; concentration of impurity = 0.020 ± 0.005 mole %.

Melted, %	1/F	T, °K. Obsd.	Graph.[a]
10.49	9.53	160.1327	160.1327
24.28	4.119	160.1557	160.1554
47.96	2.085	160.1633	160.1639
67.69	1.477	160.1664	160.1664
85.46	1.170	160.1677	160.1677
100.00	1.000		160.1684
Pure	0.000		160.1726

[a] Temperatures read from a straight line through a plot of T_{obsd} vs. 1/F.

The Vapor Pressure.—The vapor pressure of 1-butanethiol at temperatures between 51 and 136° was measured with a twin ebulliometer system that was a somewhat improved modification of the one described in an earlier publication.[17] Observations were made of the boiling and condensation temperatures of 1-butanethiol and water as the two compounds boiled simultaneously at a common pressure. The pressures corresponding to the observed boiling points of the water were obtained from the tabulation of Osborne, Stimson and Ginnings.[18] The results are presented in Table VII. The difference between the boiling and condensation temperatures of the sample was at most 0.001° at 1 atm. pressure; this observation indicates that the material was essentially free of impurities of different volatility. The constants of an Antoine equation were obtained from

$$\log_{10} p(\text{mm.}) = 6.92754 - 1281.018/(t + 218.100) \quad (4)$$

the data of Table VII by a least squares treatment.[19] Also, to provide a more accurate means of extrapolation to temperatures beyond the range of the experiments, the following Cox equation[20] was derived

$$\log_{10} P(\text{atm.}) = \text{A}(1 - 371.616/T) \quad (5)$$

where $\log_{10}\text{A} = 0.845139 - 7.0076 \times 10^{-4}\, T + 6.6593 \times 10^{-7}\, T^2$. In these equations, t is in °C. and T is in °K. Comparisons of the observed and calculated vapor pressure for both the Antoine and Cox equations are given in Table VII. The normal boiling point of 1-butanethiol, calculated from either equation, is 98.46° (371.62°K.).

The vapor pressure of 2-thiapentane was not studied experimentally, as reliable data were already available from the work of White, Barnard-Smith and Fidler.[21]

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(17) Guy 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).

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

(19) C. B. Willingham, W. J. Taylor, J. M. Pignocco and F. D. Rossini, *ibid.*, **35**, 219 (1945).

(20) E. R. Cox, *Ind. Eng. Chem.*, **28**, 613 (1936).

(21) P. T. White, D. G. Barnard-Smith and F. A. Fidler, *ibid.*, **44**, 1430 (1952).

TABLE VI

THE MOLAL THERMODYNAMIC PROPERTIES OF 1-BUTANETHIOL IN THE SOLID AND LIQUID STATES[a]

T, °K.	$-(F_{satd} - H^\circ_0)/T$, cal. deg.$^{-1}$	$(H_{satd} - H^\circ_0)/T$, cal. deg.$^{-1}$	$H_{satd} - H^\circ_0$, cal.	S_{satd}, cal. deg.$^{-1}$	C_{satd}, cal. deg.$^{-1}$
		Crystals			
10	0.033	0.097	0.97	0.130	0.387
15	.107	.315	4.72	.422	1.225
20	.247	.685	13.71	.932	2.411
25	.449	1.163	29.09	1.612	3.750
30	.709	1.707	51.22	2.416	5.100
35	1.015	2.287	80.05	3.302	6.392
40	1.359	2.877	115.08	4.236	7.607
45	1.732	3.465	155.93	5.197	8.723
50	2.126	4.046	202.28	6.172	9.803
60	2.965	5.171	310.2	8.136	11.760
70	3.843	6.239	436.7	10.082	13.482
80	4.743	7.243	579.5	11.986	15.037
90	5.651	8.191	737.2	13.842	16.476
100	6.560	9.083	908.3	15.643	17.722
110	7.466	9.923	1091.6	17.389	18.932
120	8.363	10.723	1286.7	19.086	20.087
130	9.253	11.487	1493.4	20.740	21.242
140	10.131	12.225	1711.5	22.356	22.392
150	11.000	12.942	1941.4	23.942	23.593
157.47	11.640	13.468	2120.7	25.108	24.480
		Liquid			
157.47	11.640	29.345	4621	40.99	39.19
160	12.11	29.501	4720	41.61	39.10
170	13.91	30.06	5110	43.97	38.82
180	15.65	30.54	5497	46.19	38.64
190	17.31	30.96	5883	48.27	38.53
200	18.91	31.34	6268	50.25	38.49
210	20.45	31.68	6653	52.13	38.51
220	21.93	31.99	7038	53.92	38.60
230	23.36	32.28	7425	55.64	38.76
240	24.73	32.56	7814	57.29	38.99
250	26.07	32.82	8205	58.89	39.26
260	27.37	33.07	8599	60.44	39.57
270	28.62	33.32	8997	61.94	39.93
273.16	29.00	33.40	9123	62.40	40.06
280	29.84	33.56	9398	63.40	40.35
290	31.01	33.81	9804	64.82	40.80
298.16	31.96	34.00	10,138	65.96	41.18
300	32.16	34.05	10,214	66.21	41.26
310	33.28	34.29	10,629	67.57	41.74
320	34.37	34.53	11,049	68.90	42.23

THE MOLAL THERMODYNAMIC PROPERTIES OF 2-THIAPENTANE IN THE SOLID AND LIQUID STATES[a]

T, °K.	$-(F_{satd} - H^\circ_0)/T$, cal. deg.$^{-1}$	$(H_{satd} - H^\circ_0)/T$, cal. deg.$^{-1}$	$H_{satd} - H^\circ_0$, cal.	S_{satd}, cal. deg.$^{-1}$	C_{satd}, cal. deg.$^{-1}$
		Crystals			
10	0.037	0.110	1.10	0.147	0.436
15	.122	.354	5.31	.476	1.332
20	.274	.744	14 87	1.018	2.512
25	.491	1.227	30.66	1.718	3.815
30	.762	1.770	53.11	2.532	5.162
35	1.079	2.351	82.30	3.430	6.483
40	1.432	2.946	117.86	4.378	7.736
45	1.813	3.547	159.61	5.360	8.955
50	2.218	4.145	207.26	6.363	10.097
60	3.077	5.317	319.0	8.394	12.207
70	3.982	6.438	450.6	10.420	14.040
80	4.911	7.493	599.4	12.404	15.698
90	5.852	8.489	764.0	14.341	17.185
100	6.795	9.423	942.3	16.218	18.450
110	7.735	10.299	1132.9	18.034	19.645
120	8.667	11.126	1335.1	19.793	20.773
130	9.589	11.909	1548.2	21.498	21.835
140	10.499	12.655	1771.7	23.154	22.862
150	11.397	13.370	2005.6	24.767	23.913
160	12.281	14.063	2250.0	26.344	24.982
160.17	12.297	14.075	2254.5	26.372	25.000
		Liquid			
160.17	12.297	28.865	4624	41.16	37.75
170	14.03	29.378	4994	43.41	37.75
180	15.73	29.843	5372	45.57	37.76
190	17.35	30.26	5750	47.61	37.80
200	18.91	30.64	6128	49.55	37.90
210	20.41	30.99	6508	51.40	38.01
220	21.86	31.31	6889	53.17	38.20
230	23.26	31.62	7272	54.88	38.45
240	24.61	31.91	7658	56.52	38.72
250	25.92	32.19	8046	58.11	39.03
260	27.18	32.46	8438	59.64	39.40
270	28.42	32.72	8834	61.14	39.78
273.16	28.80	32.80	8960	61.60	39.91
280	29.61	32.98	9234	62.59	40.21
290	30.77	33.24	9639	64.01	40.65
298.16	31.70	33.44	9972	65.14	41.02
300	31.91	33.49	10,047	65.40	41.11
310	33.01	33.74	10,461	66.75	41.60
320	34.08	34.00	10,879	68.08	42.11

[a] The values tabulated are the free energy function, heat content function, heat content, entropy and heat capacity of the condensed phases at saturation pressure.

TABLE VII

THE VAPOR PRESSURE OF 1-BUTANETHIOL

B.p., °C. Water	B.p., °C. 1-Butanethiol	p(obsd.),[a] mm.	p(obsd.) − p(calcd.), mm. Eq. 4	p(obsd.) − p(calcd.), mm. Eq. 5
60.000	51.409	149.41	0.00	0.00
65	57.130	187.57	− .01	.00
70	62.897	233.72	− .01	+ .01
75	68.710	289.13	− .01	+ .01
80	74.567	355.22	+ .01	.00
85	80.472	433.56	− .01	− .02
90	86.418	525.86	+ .05	+ .02
95	92.414	633.99	+ .03	.00
100	98.454	760.00	+ .06	+ .04
105	104.544	906.06	− .01	− .01
110	110.682	1074.6	− .1	− .1
115	116.863	1268.0	− .2	− .1
120	123.088	1489.1	− .1	.0
125	129.362	1740.8	.0	.0
130	135.679	2026.0	+ .3	+ .1

[a] From the vapor pressure data for water given in ref. 18.

The Heat of Vaporization.—The heat of vaporization and vapor heat capacity of both substances were studied in the flow calorimeter described in previous publications.[22] The results of measurements of the heat of vaporization at boiling points corresponding to $^1/_4$, $^1/_2$ and 1 atm. pressure are summarized in Table VIII. The estimated accuracy uncertainty of the values of ΔHv is ±0.1%. The following empirical equations were derived for interpolation in the temperature range of the measurements.

1-Butanethiol (330–372°K.)

$$\Delta Hv = 10655 - 0.4640\ T - 0.020136\ T^2 \text{ cal. mole}^{-1} \quad (6)$$

2-Thiapentane (328–369°K.)

$$\Delta Hv = 11587 - 6.4680\ T - 0.011290\ T^2 \text{ cal. mole}^{-1} \quad (7)$$

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(22) (a) Guy Waddington, S. S. Todd and H. M. Huffman, THIS JOURNAL, **69**, 22 (1947); (b) J. P. McCullough, D. W. Scott, R. E. Pennington, I. A. Hossenlopp and Guy Waddington, *ibid.*, **76**, 4791 (1954).

The Vapor Heat Capacity and the Effects of Gas Imperfection.—The vapor heat capacity of each substance was measured at two or more pressures at each of five temperatures between 360 and 500°K. The results are summarized in Table IX.

TABLE VIII

THE MOLAL HEATS OF VAPORIZATION AND SECOND VIRIAL COEFFICIENTS

T, °K.	P, atm.	ΔH_v, cal.	B_{obsd}, cc.	B_{calcd}, cc.[a]
		1-Butanethiol		
330.62	0.250	8301 ± 1[b]	−1615	−1585
349.70	0.500	8030 ± 4[b]	−1431	−1407
371.62	1.000	7702 ± 1[b]	−1243	−1262
		2-Thiapentane		
328.12	0.250	8249 ± 2[b]	−1663	−1688
347.02	0.500	7983 ± 2[b]	−1452	−1444
368.70	1.000	7667 ± 1[b]	−1233	−1230

[a] Calculated with eq. 9 or 10. [b] Maximum deviation from the mean of three or more determinations.

TABLE IX

THE MOLAL VAPOR HEAT CAPACITY IN CAL. DEG.$^{-1}$

1-Butanethiol

T, °K.	360.20	382.20	417.20	453.20	500.20
C_p(1.000 atm.)		34.521	36.480	38.549	41.162
C_p(0.500 atm.)	32.826	34.138			
C_p(0.250 atm.)	32.583	33.993	36.178	38.355	41.064
$C_p°$(obsd.)	32.35	33.82	36.08	38.29	41.03
[C_p(1 atm.) − $C_p°$](obsd.)		0.70	0.40	0.26	0.13
[C_p(1 atm.) − $C_p°$](calcd.)[a]		0.69	0.40	0.25	0.14

2-Thiapentane

T, °K.	375.20	400.20	433.20	466.20	500.20
C_p(1.000 atm.)	33.968	35.296	37.154	39.012	40.864
C_p(0.500 atm.)	33.482				
C_p(0.250 atm.)	33.275	34.788	36.824	38.748	40.685
$C_p°$(obsd.)	33.05	34.63	36.72	38.66	40.63
[C_p(1 atm.) − $C_p°$](obsd.)	0.92	0.67	0.43	0.35	0.23
[C_p(1 atm.) − $C_p°$](calcd.)[a]	0.92	0.67	0.45	0.33	0.24

[a] Calculated with eq. 8 and 9 or 10.

To correlate the thermal data, equations of state were obtained from data for the vapor pressure, heat of vaporization and vapor heat capacity. Values of the second virial coefficient, B, in the equation of state, $PV = RT(1 + B/V)$, were computed by use of the exact Clapeyron equation. Values of $\mathrm{d}^2B/\mathrm{d}T^2$ were determined from the thermodynamic relationship, $(\partial^2 V/\partial T^2)_P = -1/T(\partial C_p/\partial P)_T$, in terms of which the variation of vapor heat capacity with pressure is represented, with slight approximations,[22b] by

$$C_p = C_p° - T\left(\frac{\mathrm{d}^2B}{\mathrm{d}T^2}\right)P + 2\left(\frac{B}{R}\right)\left(\frac{\mathrm{d}^2B}{\mathrm{d}T^2}\right)\left(1 - \frac{3BP}{RT}\right)P^2 \quad (8)$$

The numerical constants of the empirical equations for B were determined by the method described in ref. 22b.

1-Butanethiol (330–500°K.)

$$B = -668 - 17.97 \exp(1300/T) \text{ cc. mole}^{-1} \quad (9)$$

2-Thiapentane (328–500°K.)

$$B = 70 - 113.2 \exp(900/T) \text{ cc. mole}^{-1} \quad (10)$$

Values of B, computed by use of eq. 9 and 10, and values of C_p(1 atm.) − $C_p°$, computed by use of eq. 8 and 9 or 10, are compared with the experimental values in Tables VIII and IX, respectively.

To determine the "observed" values of $C_p°$ listed in Table IX, the last term in eq. 8 was evaluated for each experimental point by use of eq. 9 or 10 and then subtracted from C_p(obsd.).[23] The adjusted values of C_p at each temperature were then extrapolated linearly to zero pressure to obtain $C_p°$(obsd.). The accuracy uncertainty of the values of $C_p°$(obsd.) listed in Table IX should not exceed 0.2%. The following empirical equations represent these data within ±0.06%.

1-Butanethiol (360–500°K.)

$$C_p° = 2.628 + 9.7293 \times 10^{-2}T - 4.1015 \times 10^{-5}T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (11)$$

2-Thiapentane (375–500°K.)

$$C_p° = 3.652 + 9.1600 \times 10^{-2}T - 3.5347 \times 10^{-5}T^2 \text{ cal. deg.}^{-1} \text{ mole}^{-1} \quad (12)$$

The Entropy in the Ideal Gaseous State.—The experimental and derived results given in the foregoing sections were used to compute "observed" values of the entropy in the ideal gaseous state at 1 atm. These calculations are summarized in Table X.

TABLE X

THE MOLAL ENTROPY IN CAL. DEG.$^{-1}$

1-Butanethiol

0–10°K.	Debye extrapolation[a]	0.130
10–157.47°	Crystals, $\int C_{\text{satd}}\, \mathrm{d} \ln T$	24.978
157.47°	Fusion, 2500/157.47	15.876
157.47–298.16°	Liquid, $\int C_{\text{satd}}\, \mathrm{d} \ln T$	24.972
S_{satd}(liq.), 298.16°K. (±0.13)[b]		65.96

T, °K.	330.62	349.70	371.62
S_{satd}(liq.)[c]	70.29	72.73	75.43
$\Delta H_v/T$[d]	25.11	22.96	20.72
S(ideal) − S(real)[e]	0.06	0.10	0.15
$R \ln (p/760)$[f]	−2.75	−1.38	0.00
$S°$(obsd.)(±0.20)[b]	92.71	94.41	96.30

2-Thiapentane

0–10°K.	Debye extrapolation[a]	0.147
10–160.17°	Crystals, $\int C_{\text{satd}}\, \mathrm{d} \ln T$	26.225
160.17°	Fusion, 2369/160.17	14.791
160.17–298.16°	Liquid, $\int C_{\text{satd}}\, \mathrm{d} \ln T$	23.982
S_{satd}(liq.), 298.16°K. (±0.13)[b]		65.14

T, °K.	328.12	347.02	368.70
S_{satd}(liq.)[c]	69.14	71.55	74.22
$\Delta H_v/T$[d]	25.14	23.00	20.79
S(ideal) − S(real)[e]	0.09	0.15	0.22
$R \ln (p/760)$[f]	−2.75	−1.38	0.00
$S°$(obsd.)(±0.20)[b]	91.62	93.32	95.23

[a] $5/3D(125.8/T)$ for 1-butanethiol and $3/2D(116.5/T)$ for 2-thiapentane. [b] Estimated accuracy uncertainty. [c] Extrapolated by use of eq. 1 and 2. [d] Entropy of vaporization; calculated from data of Table VIII. [e] Entropy of gas imperfection; calculated by use of eq. 9 and 10. [f] Entropy of compression to 1 atm.; calculated by use of eq. 5 and data of ref. 21.

The Heat of Formation and Related Properties.—The heat of formation of each substance was determined by a rotating-bomb method of combustion calorimetry.[24] Detailed description of the experiments is planned for inclusion in another publication, and only the pertinent results are reported here. Values of the standard heat of formation of the liquid are tabulated below, along with values of the standard entropy, standard free energy and logarithm of the equilibrium constant of formation. The latter were calculated by

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[23] The maximum value of the last term in eq. 8 was 0.10 cal. deg.$^{-1}$ mole^{-1} for 1-butanethiol and 0.07 cal. deg.$^{-1}$ mole^{-1} for 2-thiapentane.

[24] W. N. Hubbard, C. Katz and Guy Waddington, *J. Phys. Chem.*, **58**, 142 (1954).

$4C(\text{graphite}) + 5H_2(g) + S(\text{rhombic}) = C_4H_{10}S(\text{liq})$

	$\Delta Hf°_{298.16}$, kcal. mole^{-1}	$\Delta Sf°_{298.16}$, cal. deg.$^{-1}$ mole^{-1}	$\Delta Ff°_{298.16}$, kcal. mole^{-1}	$\log_{10} Kf_{298.16}$
1-Butanethiol	−29.61 ± 0.28	−103.16	+1.15	−0.84
2-Thiapentane	−28.03 ± .22	−103.98	+2.97	−2.18

The standard heat of vaporization, $\Delta H_v°_{298.16}$, was calculated by use of eq. 5, 6, 7, 9 and 10, the data of ref. 21, and the relationship, $\Delta Hv° = \Delta H_v - BRT/V + (dB/dT) \cdot RT^2/V$. The values obtained were 8.74 kcal. mole^{-1} for 1-butanethiol and 8.67 kcal. mole^{-1} for 2-thiapentane.

use of values of entropy from Table X and the thermodynamic functions for C(graphite),[8] $H_2(g)$[8] and S (rhombic).[25]

The foregoing values of the heat of vaporization were used to obtain the values of the standard heat of formation of the gas tabulated below. Also tabulated are values of the standard entropy, standard free energy and logarithm of the equilibrium constant of formation, calculated by use of values of entropy from Tables II and III.

$4C(\text{graphite}) + 5H_2(g) + S(\text{rhombic}) = C_4H_{10}S(g)$

	$\Delta Hf°_{298.16}$, kcal. mole^{-1}	$\Delta Sf°_{298.16}$ cal. deg.$^{-1}$ mole^{-1}	$\Delta Ff°_{298.16}$, kcal. mole^{-1}	$\log_{10} Kf_{298.16}$
1-Butanethiol	−20.87 ± 0.29	−79.44	+2.82	−2.06
2-Thiapentane	−19.36 ± .23	−80.28	+4.58	−3.35

The heat of formation of $S_2(g)$ from rhombic sulfur[9] was used to compute values of the heat of formation from $S_2(g)$, as given in Table I.

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[25] F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," N. B. S. Circular 500, 1952, Series, 1, Table 14-1.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

Molecular Addition Compounds of Titanium Tetrabromide and Titanium Tetraiodide with Several Ethers

BY ROBERT F. ROLSTEN AND HARRY H. SISLER[1]

RECEIVED JULY 30, 1956

The reactions of titanium tetrabromide and titanium tetraiodide with 1,4-dioxane, tetrahydrofuran and tetrahydropyran have been studied and the new compounds $TiBr_4 \cdot O(CH_2CH_2)_2O$, $TiBr_4 \cdot 2C_4H_8O$ and $TiBr_4 \cdot 2C_5H_{10}O$ have been isolated. No pure addition compound of titanium tetraiodide with any one of the ethers could be isolated. It is believed that splitting of the ethers occurs in the presence of the tetraiodide and to some extent with the tetrabromide.

Introduction

Previous publications from this Laboratory[2-4] have shown that whereas tin and titanium tetrachlorides readily form stable, solid molecular addition compounds with various ethers, silicon and germanium tetrachlorides do not do so. The formation of tin tetrachloride addition compounds was interpreted as resulting from Lewis acid–base reactions in which the metal atom expanded its valence shell by accepting a pair of electrons from an oxygen atom of each of two molecules of ether to form compounds of the general type $MCl_4 \cdot 2R_2O$. The failure of silicon and germanium tetrachlorides to form such compounds was attributed to the size of the chlorine atom being such as to cause four of these atoms to fill so completely the coördination sphere of the silicon and germanium atoms, as to prevent any reaction with the ether. This is in line with the measurements[5] of the dipole moments of solutions of silicon, germanium and tin tetrachlorides in dioxane, which indicate that the extent of coördination with the dioxane increases in the sequence $SiCl_4 < GeCl_4 > SnCl_4$.

It was decided, therefore, to determine the effect, if any, of the replacement of the chlorine atoms in titanium tetrachloride by larger halogens, on the tendency for titanium tetrahalides to react with ethers.

Experimental

Preparation and Purification of Materials.—Titanium used for preparing the tetrabromide and tetraiodide was prepared and purified by the method of Campbell, *et al.*,[6] and was shown spectroscopically to contain less than 0.1% metallic impurity. C.P. grades of bromine and iodine were used without further purification.

Titanium tetrabromide was prepared and purified by the method of Blocher and Rolsten[7] from pure titanium metal and liquid bromine and its purity checked by analysis. *Anal.* Calcd. for $TiBr_4$: Ti, 13.03; Br, 86.97. Found: Ti, 13.2, 13.1; Br, 86.8, 86.7.

Titanium tetraiodide was prepared by the direct reaction of gaseous iodine and excess titanium metal in the absence of air and moisture. It was purified by distillation and stored over P_4O_{10} in a desiccator. *Anal.* Calcd. for TiI_4: Ti, 8.62; I, 91.38. Found: Ti, 8.55, 8.71; I, 91.4, 89.0, 89.7.

The 1,4-dioxane was purified by the method of Fieser.[8] Tetrahydrofuran and tetrahydropyran were dried over calcium chloride, and then fractionated from over sodium in a dry argon atmosphere using a five-foot column packed with glass helices. A constant boiling middle fraction was retained. Boiling point data: C_4H_8O, 65.2–65.6° (743 mm.); 1,4-dioxane, 100.3–100.7° (744 mm.); $C_5H_{10}O$, 87.5–88.5° (746 mm.). The 1,4-dioxane froze at 11.57°. To avoid the presence of peroxides which these ethers form readily, they were prepared immediately before use.

Preparation of $TiBr_4 \cdot C_4H_8O_2$.—Titanium tetrabromide was allowed to react with an excess of carefully dried 1,4-dioxane in a closed system under an atmosphere of dry argon. During the reaction the dioxane was kept at a tem-

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[1] Department of Chemistry, University of Florida, Gainesville, Florida.

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[3] H. H. Sisler, H. H. Batey, B. Pfahler and R. Mattair, *ibid.*, **70**, 3821 (1948).

[4] H. H. Sisler, P. M. Hamilton, R. McBeth and W. Bekebrede, *ibid.*, **75**, 2881 (1953).

[5] T. J. Lane, P. A. McCusker and B. C. Curran, *ibid.*, **64**, 2076 (1942).

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