As far as the fluorescence property is concerned, R_6 resembles deuteroporphyrin more than R_2, R_3, etc. In NaOH solution, its fluorescence disappears almost at the same rate as that of deuteroporphyrin; but in organic solvents it is not as thermostable as that of the latter. For instance, it loses its fluorescence considerably even at 105°. R_3 is also very unstable around this temperature, changing partly into the more stable R_2.

HCl numbers of these products and absorption data of the copper complex of R_2 ester are listed together in Table I.

Discussion

The absorption data of these porphyrin products indicate the absence of vinyl groups. This point has been supplemented by the negative qualitative test for the vinyl group.[5] Although R_2 is most probably an intermediate in the formation of deuteroporphyrin, it is not 4-vinyldeuteroporphyrin,[6] spirographisporphyrin,[7] monoformyl or diformyl deuteroporphyrin,[8] as evidenced by the spectroscopic data and negative chemical tests toward the reagents, diazoacetic methyl ester and hydroxylamine.

The different trends noted in the fluorescence changes of the group (Fig. 2B) are shown by the NaOH reaction. With a 4% NaOH, they give R_6 and deuteroporphyrin as the main fluorescent products. As shown in Fig. 2A, these porphyrins have more intense fluorescence in the strongly alkaline region. On the other hand a reacting medium with *p*H between 6–11 is favorable for the formation of non-fluorescent products.

The results of the NaOH reaction which may be outlined as $R_5 \rightarrow R_2(R_3) \rightarrow R_6 +$ deutero, support the view that they are most likely the precursors of deuteroporphyrin IX and should play some roles in the mechanism of the formation of deuteroporphyrin by the resorcinol fusion.

The authors wish to express their appreciation to Sister Agnes Ann Green for her interest in the work.

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[5] E. J.-H. Chu, *J. Biol. Chem.*, **166**, 463 (1946).

[6] H. Fischer and G. Wecker, *Z. physiol. Chem.*, **272**, 1 (1941).

[7] H. Fischer and H. Orth, "Die Chemie des Pyrrols," Vol. II, 1937, p. 468.

[8] Ref. 7, p. 292.

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Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Stannic and Stannous Sulfides

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Existing thermodynamic information on the sulfides of tin is rather meager, and low-temperature heat-capacity and entropy data have been entirely lacking. This paper presents the results of low-temperature heat capacity measurements of both stannic and stannous sulfides, with an evaluation of their entropies at 298.16°K.

Materials.—The stannic sulfide was prepared by K. R. Bonnickson of this Laboratory from reagent-grade stannous chloride dihydrate, sulfur and ammonium chloride. These ingredients were mixed in the molal proportion of 1:3:2 and heated in an open-end tube, first at 150° until evolution of water ceased and then for three hours at 300–350°, after which the tube was stoppered and cooled. The reaction mass was broken up, shaken with water, and centrifuged four times. It was then shaken with alcohol, centrifuged and dried at 60°. Finally the product was mixed with 10% by weight of sulfur and heated in vacuum for five hours at 300°, the excess sulfur being distilled off in the process. The product analyzed 64.95% tin, as compared with the theoretical 64.92%. The X-ray diffraction pattern agreed with that given for stannic sulfide in the A.S.T.M. catalog, except for the presence of four weak lines that could not be identified.

The stannous sulfide was furnished by M. J. Spendlove of the College Park, Md., Station of the Bureau of Mines. It was prepared by adding sulfur to an excess of molten tin, skimming off the reaction product, and roasting at 980° to remove excess sulfur and produce a crude grade of stannous sulfide. The crude material then was purified by sublimation in vacuum, which gave a well crystallized, dense product. Chemical analysis showed the substance to contain 99.2% stannous sulfide and 0.6% stannic oxide, leaving about 0.2% unaccounted for. Spectrographic analysis indicated less than 0.01% each of aluminum, bismuth, iron, magnesium, calcium, sodium and copper, while silicon and lead may run as high as 0.05%.

Measurements and Results.—The measurements were conducted with previously described apparatus.[1] The sample masses employed were 104.12 g. of stannic sulfide and 338.98 g. of stannous sulfide. The stannous sulfide results were corrected for the 0.6% stannic oxide content by means of the heat capacity data of Millar,[2] the correction ranging from 0.38% at the lowest temperature to zero at the highest. No correction of the stannic sulfide results was necessary.

The measured heat capacities appear in Table I, being expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole. Molecular weights accord with the 1951 International Atomic Weights.[3]

TABLE I

HEAT CAPACITIES

T, °K.	C_p, cal./deg. mole	*T*, °K.	C_p, cal./deg. mole	*T*, °K.	C_p, cal./deg. mole
		SnS_2 (mol. wt., 182.83)			
52.75	4.139	114.65	10.24	216.55	15.16
56.45	4.453	124.72	11.02	226.55	15.38
60.65	4.874	135.98	11.80	236.88	15.62
65.17	5.389	146.13	12.43	246.21	15.84
70.05	5.900	155.79	12.92	257.06	16.02
74.92	6.407	166.54	13.44	266.82	16.21
80.28	6.976	176.14	13.85	276.28	16.39
84.04	7.387	186.22	14.24	287.38	16.58
93.66	8.356	196.28	14.56	296.54	16.76
105.07	9.435	206.63	14.87	(298.16)	(16.76)
		SnS (mol. wt., 150.77)			
52.45	4.762	114.70	8.837	216.37	11.10
56.82	5.115	125.28	9.249	226.05	11.19
61.40	5.525	136.01	9.607	236.31	11.28
65.90	5.920	146.22	9.901	246.03	11.37
70.49	6.277	155.93	10.13	256.19	11.45
75.28	6.623	166.03	10.34	266.05	11.55
80.20	6.974	176.12	10.54	276.36	11.61
83.71	7.208	186.09	10.69	286.68	11.69
94.67	7.868	195.91	10.84	296.80	11.77
104.47	8.368	206.31	10.95	(298.16)	(11.77)

Both substances exhibit normal heat capacity curves. The only unusual feature is that, at tem-

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[1] K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

[2] R. W. Millar, THIS JOURNAL, 51, 207 (1929).

[3] E. Wichers, *ibid.*, 74, 2447 (1952).

peratures below 80°K., the stannic compound has the lower molal heat capacity, despite the extra atom of sulfur in its molecular composition. A similar phenomenon is evident in Millar's[2] results for stannic and stannous oxides, the former having the lower molal heat capacity at temperatures below about 155°K.

Entropies at 298.16°K.—The entropy increments for the measured temperature range, 51.00 to 298.16°K., were obtained by Simpson-rule integrations of plots of C_p against log T. The extrapolated portions, between zero and 51.00°K., were evaluated by means of the following empirical sums of Debye and Einstein functions which fit the measured heat capacities to within the limits and for the temperature ranges shown in parentheses.

$$\mathrm{SnS_2}: D(172/T) + E(369/T) + E\left(\frac{415}{T}\right)\ (1.0\%,\ 51\text{–}170\text{°K.})$$

$$\mathrm{SnS}: \quad D(146/T) + E(311/T)\ (1.0\%,\ 51\text{–}150\text{°K.})$$

Results of the entropy calculations are in Table II. The measured portions constitute 89.7 and 84.5%, respectively, of the totals at 298.16°K. for stannic and stannous sulfides.

TABLE II

ENTROPIES AT 298.16°K. (CAL./DEG. MOLE)

	SnS_2	SnS
0–51°K. (extrap.)	2.15	2.84
51–298.16°K. (meas.)	18.78	15.52
$S°_{298.16}$	20.9 ± 0.2	18.4 ± 0.2

Employing entropy values for white tin and rhombic sulfur listed by Kelley,[4] the entropies of formation of stannic and stannous sulfides are, respectively, $\Delta S_{298.16} = -6.6 \pm 0.2$ and $\Delta S_{298.16} = -1.5 \pm 0.2$ cal./deg. mole.

[4] K. K. Kelley, U. S. Bur. Mines Bulletin 477 (1950).

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Decomposition of Nitrosyl Disulfonate Ion. II. The Relation to the Mechanisms of Diazotization and Deamination

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In connection with the study of the decomposition of nitrosyl disulfonate ion,[1] we have studied the reaction of nitrous acid with nitrosyl disulfonate ion and with sulfamate ion[2]; and we have found both cases significantly related to the mechanisms proposed for diazotization and deamination.

The first reaction in one molar sodium acetate solution was kinetically second order with respect to molecular nitrous acid and zero order to nitrosyl disulfonate ion. This rate law was deduced from the concentration and pH dependence of the rate of disappearance of the colored nitrosyl disulfonate ion and the evolution of nitrous oxide product.

As one evidence for the validity of the treatment the dissociation constant of nitrous acid was obtained from a plot of $1/\sqrt{k}$ *vs.* $1/[\mathrm{H}^+]$ as required by the relation

$$\frac{1}{\sqrt{k}} = \frac{K}{\gamma_-\sqrt{k'}} \cdot \frac{1}{[\mathrm{H}^+]} + \frac{1}{\sqrt{k'}} \qquad (1)$$

In equation (1) k is the rate constant at a given pH, K the dissociation constant of nitrous acid, γ_- the activity coefficient of NO_2^- and k' the pH independent constant for the proposed rate law: rate = $k'(\mathrm{HNO_2})$.[2] The value obtained was $5 \pm 0.5 \times 10^{-4}\ \gamma_-$ close to $5.15 \times 10^{-4}\ \gamma_\pm^2$ obtained by Schmid, Marchgraber and Dunkl[3] at 25°.

Following Hammett's suggestion[4] for the second-order participation of nitrous acid, we have deduced the following mechanism

$$2\mathrm{HNO_2} \xrightarrow{k_1} \mathrm{N_2O_3} + \mathrm{H_2O}$$

$$(\mathrm{SO_3})_2\mathrm{NO}^{=} + \mathrm{N_2O_3} + 2\mathrm{H_2O} \xrightarrow{\text{fast}} 2\mathrm{SO_4}^{=} + \mathrm{NO}^+ + \mathrm{NO} + \mathrm{NOH} + \mathrm{H_3O}^+$$

$$(\mathrm{SO_3})_2\mathrm{NO}^{=} + \mathrm{NO} + \mathrm{H_3O}^+ \xrightarrow{\text{fast}} (\mathrm{SO_3})_2\mathrm{NOH}^{=} + \mathrm{NO}^+ + \mathrm{H_2O}$$

with NO^+ and 2NOH giving nitrous acid and nitrous oxide, respectively. The rate constant k_1 = 7,000 l./mole-min. was obtained at 25°. From the temperature dependence of k_1 between 35 and 10°, k_1 = 300 was obtained at 0° by extrapolation.

Compare this reaction with the diazotization of aniline[5] at 0° and mild acidity where the concentration dependences were zero order for amine and second order for nitrous acid. In the calculation, a value[3] of 3.55×10^{-4} was used for the dissociation constant of nitrous acid at 0° and the activity coefficient of NO_2^- was taken as 0.8 in the phthalate buffer solution. The following table shows results of calculations based upon data transcribed from the latter paper

pH	Rate/$(\Sigma\ \mathrm{HNO_2})^2$	$[1 + (K/[\mathrm{H}^+]\gamma^-)]^2$	k_1
4.80	0.30	840	252
5.00	.14	2060	289
5.20	.063	5100	321

The agreement suggests that N_2O_3 is the actual reacting species in the acid decomposition of nitrosyl disulfonate ion as well as in some diazotization reactions.

The second reaction between sulfamate ion and nitrous acid was found kinetically first order with respect to each reactant in an acetate buffer solution, and the pH dependence showed the following rate law at 25° and 0.17 ionic strength

$$\frac{d(\mathrm{N_2})}{dt} = 7.0 \times 10^4(\mathrm{HNO_2})(\mathrm{H}^+)(^-\mathrm{SO_3NH_2})\ \text{moles/liter-min.}$$

in agreement with Dusenbury and Powell[6] who suggested NO^+ or $H_2NO_2^+$ as the deamination agent.

We also have re-examined[7] the data of Taylor[8]

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[1] J. H. Murib and D. M. Ritter, THIS JOURNAL, **74**, 3394 (1952).

[2] Forthcoming papers III, IV of this series.

[3] H. Schmid, R. Marchgraber and F. Dunkl, *Z. Elektrochem.*, **43**, 337 (1937).

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 294.

[5] E. D. Hughes, C. K. Ingold and J. H. Ridd, *Nature*, **166**, 642 (1950).

[6] J. H. Dusenbury and R. E. Powell, THIS JOURNAL, **73**, 3266, 3269 (1951).

[7] See also, A. T. Austin, E. D. Hughes, C. K. Ingold and J. H. Ridd, *ibid.*, **74**, 555 (1952).

[8] T. W. J. Taylor, *J. Chem. Soc.*, 1099, 1897 (1928).