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The Pyrolysis of Heptathiazocine

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Heptathiazocine was pyrolyzed into ammonia, tetrasulfur tetranitride, and tetrasulfur dinitride above 383 K in an argon atmosphere; then, the latter two intermediates finally degraded into sulfur and nitrogen. According to the stoichiometric correlation among the final pyrolytic products, an overall pyrolysis can be expressed as: $S_7NH=7/8\,S_8+1/3\,N_2+1/3\,NH_3$. The differential scanning calorimetry of heptathiazocine gave the standard enthalpy of the formation as $89._3\pm1._1$ kJ mol^{-1} by combining the enthalpy change of the pyrolysis with its molar heat capacity and known thermodynamic data of the concerned species. The standard enthalpies of the formation of this compound were also calculated as being 93 and 91 kJ mol^{-1} on the basis of Sanderson's method, assuming that hydrogen bonds were negligible in the crystal (which were comparable to that observed in this work).

Heptathiazocine (heptasulfur imide, S_7NH) is a stable compound at room temperature with a melting point of 386.7 K.[1,2] This compound is soluble in various organic solvents, of which the solubility parameter has been estimated in a previous paper.[1] Little information on the pyrolysis of this compound is available, though heptathiazocine decomposes above its melting point.[3] Becke-Goehring and Schwarz[4] have estimated its standard enthalpy of formation on the basis of pyrolysis in vacuo.

In this work, the pyrolysis of heptathiazocine was studied within the temperature range 353—513 K under an argon atmosphere in order to verify the thermal decomposition process and the thermodynamic quantities.

Experimental

Materials. The heptathiazocine was prepared by a method described by Heal and Kane,[5] followed by purification by repeated recrystallization and column chromatography.[1] Thin-layer chromatography (TLC) showed that the heptathiazocine, thus obtained, was sufficiently pure to use in this work.

Procedures. Differential thermal analysis (DTA) and thermal gravimetry (TG) on the heptathiazocine were carried out at heating rates of 3—15 K min^{-1} in an argon atmosphere with a Rigaku Denki Thermoflex (model 8002). Pyrolytic products of the heptathiazocine were identified by TLC[6] and with a Yanagimoto Seisakusho (model 80) gas chromatograph.

The stoichiometric correlation among the pyrolytic products was estimated as follows: The sample (≈300 mg) was heated at 433 K for 2 h in an argon flow (25 cm^3 min^{-1}). The ammonia produced was introduced together with argon into 4.04×10^{-2} mol dm^{-3} perchloric acid and then titrated with a 3.06×10^{-2} mol dm^{-3} sodium hydroxide solution. The quantity of nitrogen was estimated with an azotometer after the accompanying ammonia was removed by passing it through 0.5 mol dm^{-3} perchloric acid, while carbon dioxide was used as a carrier gas. Respective amounts of the residual heptathiazocine and solid pyrolytic products were determined spectrophotometrically at different wavelengths using their carbon tetrachloride solution.

The molar heat capacity of heptathiazocine and the enthalpy change of the decomposition were estimated at heating rates of 8 and 16 K min^{-1} with a Perkin-Elmer (model DSC-1B) differential scanning calorimeter. The sample was carefully weighed and sealed by the same method described in a previous paper.[7] The DSC instrument was calibrated with indium of 99.999% purity; quartz was used as a reference for the measurement of the molar heat capacity.

Results

Pyrolytic Products and Differential Thermal Analysis. The heptathiazocine (≈2 mg) sealed under the argon atmosphere was heated at the heating rate of 7.5 K min^{-1} up to the specified temperatures. The remaining solid was dissolved in carbon tetrachloride and identified by TLC (Table 1). Tetrasulfur tetranitride (S_4N_4) and tetrasulfur dinitride (S_4N_2) were observed as intermediates above 413 K under these conditions, whereas these two nitrides completely degraded into sulfur and nitrogen above 453 K. The heptathiazocine did not degrade below its melting point (386.7 K)[2] by rapid heating faster than 5 K min^{-1}. However, this compound obviously decomposed, even at 383 K, by prolonged heating for 1.5 h in an argon atmosphere.

Table 1. Solid Pyrolytic Products of Heptathiazocine at Different Temperatures[a)]

T/K	Specie			
383	S_7NH			
393	S_7NH	S_8[b)]		
403	S_7NH	S_8		
413	S_7NH	S_8	S_4N_4[b)]	S_4N_2[b)]
423	S_7NH	S_8	S_4N_4	S_4N_2
433	S_7NH	S_8	S_4N_4	S_4N_2
443	S_7NH	S_8	S_4N_4	S_4N_2
453	S_7NH	S_8		
463		S_8		

a) Heating rate of 7.5 K min^{-1}. b) Trace amount.

Nitrogen and ammonia were detected as gaseous products above 413 K by gas chromatography. Hydrogen sulfide was not detectable under the conditions applied in this work.

Table 2 shows the molar ratios of the final pyrolytic products to the original heptathiazocine upon heating at 433 K for 2 h. However, trace amounts of the tetrasulfur tetranitride and tetrasulfur dinitride were still detectable as $n(S_4N_4)/n(S_7NH)=5\times10^{-3}$ and $n(S_4N_2)/n(S_7NH)\approx1\times10^{-4}$, respectively, even under the conditions. As shown in Table 1, these two nitrides finally decomposed into sulfur and nitrogen.[8] Thus, the corresponding amounts of sulfur and nitrogen were taken into account to the molar ratios in Table 2. The stoichiometric correlation clearly indicated that the overall pyrolysis of heptathiazocine could be expressed as[9]

$$S_7NH = 7/8\,S_8 + 1/3\,N_2 + 1/3\,NH_3. \qquad (1)$$

A differential thermal analysis of the heptathiazocine showed a sharp endothermic peak due to its fusion at 387 K and a broad exothermic peak at 430 K in an argon atmosphere at a heating rate of 10 K min^{-1} (as also shown in the DSC pattern (Fig. 1)). These peak temperatures shifted from 387 to 390 K and from 423 to 440 K, respectively, upon increasing the heating rate from 3 to 15 K min^{-1}. The TG curve obtained at a heating rate of 10 K min^{-1} showed a weight loss of about 6% between 398 and 443 K (Fig. 1). This weight loss approximately corresponded to a total mass of NH groups in the heptathiazocine molecules. As is also clearly shown in the gas-chromatographic analysis, these NH groups were partly converted to ammonia and nitrides.

Table 2. Molar Ratios of Final Pyrolytic Products of Heptathiazocine at 433 K

$n(S_7NH)$/mmol	Molar ratio of pyrolytic product $n(S_8)/n(S_7NH)$	 $n(N_2)/n(S_7NH)$	 $n(NH_3)/n(S_7NH)$
1.26	0.88_0	—	0.32_3
1.25	0.88_7	—	0.32_5
1.31	0.85_5	—	0.33_8
1.18	0.89_0	0.33_6	—
1.05	0.87_7	0.33_4	—
1.18	0.84_6	0.31_8	—
Average[a)]	$0.87_3\pm0.02_2$	$0.32_9\pm0.01_7$	$0.32_9\pm0.01_4$

a) The uncertainty value was defined as $\pm3.0\,\sigma/\sqrt{n}$, where σ and n are the standard deviation and the number of data respectively.

Heat Capacity of Heptathiazocine. In order to determine the heat capacity, the sample was sealed in an aluminium container under an argon atmosphere. Measurements were carried out at a heating rate of 8 K min^{-1} between 328 and 368 K. The sample, thus heated, did not show any chemical change according to TLC, even after each run for 20 min. Figure 2 shows the molar heat capacity of heptathiazocine as a function of temperature. This procedure was confirmed to be reasonably reliable by comparing the molar heat capacities of α-sulfur[10] with those observed under the same conditions (±1.4%). The molar heat capacity of heptathiazocine at 298.15 K was deduced as 0.196±0.004 kJ mol^{-1}K^{-1} from a linear relationship in the given temperature range (C_p= $0.135+2.05\times10^{-4}T$) as shown in Fig. 2.

Enthalpy Change during Pyrolysis of Heptathiazocine in Argon Atmosphere. The enthalpy change during the overall pyrolysis of heptathiazocine was measured over a temperature range from 353 to 513 K in a closed system. Figure 1 shows the DSC pattern of the heptathiazocine obtained at a heating rate of 8 K min^{-1}, in addition to the base line (dotted line) taken in this work. Table 3 indicates the results of the enthalpy changes of the fusion, ΔH_{fus}, and of the thermal decomposition, ΔH, of the heptathiazocine, in which the average values were estimated as being 18.8±0.6 and $-104._9\pm1._1$ kJ mol^{-1}, respectively.

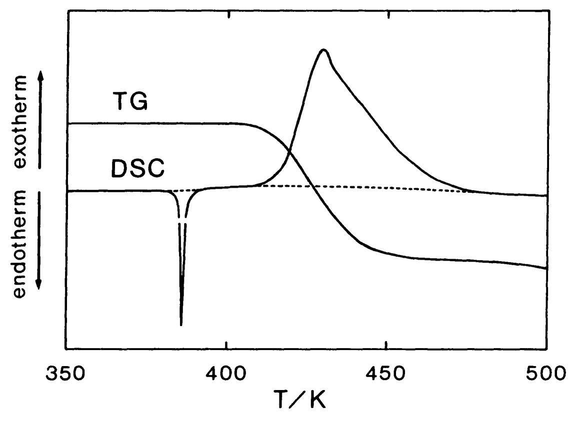

Fig. 1. DSC and TG patterns of heptathiazocine in argon atmosphere.

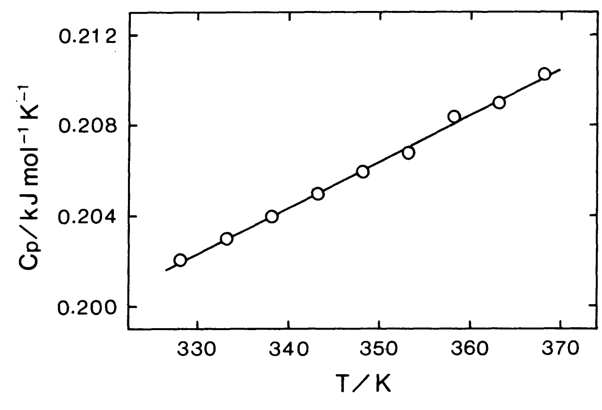

Fig. 2. Molar heat capacity of heptathiazocine observed at heating rate of 16 K min^{-1}.

Table 3. Enthalpy Changes of Fusion and Decomposition of Heptathiazocine

$n(S_7NH)$ / μmol	ΔH_{fus} / kJ mol^{-1}	$-\Delta H$ / kJ mol^{-1}
3.94	19.4	$105._0$
5.16	18.8	$104._2$
5.59	18.9	$107._2$
4.89	19.2	$105._7$
5.33	19.0	$104._7$
4.89	19.3	$104._1$
4.86	18.6	$104._7$
4.88	18.1	$103._5$
5.65	17.6	$104._8$
Average[a]	18.8 ± 0.6	$104._9\pm1._1$

a) The uncertainty value was shown in the same manner in Table 2.

On the basis of the stoichiometric correlation (Eq. 1), the standard enthalpy of the formation of heptathiazocine can be obtained by the following equation as:

$$\Delta H_f(S_7NH, s, 298.15\ K) = -\Delta H - \Delta H_{fus} + 2/3\,RT + 7/8(\Delta H_t(\alpha,\beta) + \Delta H_m(\beta,\lambda) + X\Delta H_p) + 1/3\,\Delta H_f(NH_3, g, 298.15\ K) - \int_{298.15}^{T} \Delta C_p dT \qquad (2)$$

where $\Delta H_t(\alpha,\beta)$ and $\Delta H_m(\beta,\lambda)$ are the enthalpy changes of the transition from S_α to S_β (3.2 kJ mol^{-1})[10,11] and of the fusion of S_β (13.8 kJ mol^{-1}),[10,11] ΔH_p the enthalpy change of the polymerization from S_λ to S_μ (13.3 kJ mol^{-1}),[10,11] X the fraction of S_μ as the S_8 unit,[10,12] $\Delta H_f(NH_3, g, 298.15\ K)$ the standard enthalpy of the formation of ammonia (−45.9 kJ mol^{-1}),[11] and ΔC_p the difference in the molar heat capacities between the initial and final states, respectively. The reaction temperature, T, was taken as 429 K at the maximum of broad exothermic peak (Fig. 1). The integral term was calculated as 0.1 kJ mol^{-1} using the observed molar heat capacity of heptathiazocine. However, the peak temperature (429 K) was just below the initiation temperature (432 K)[12] of rapid polymerization of S_λ. Thus, the fraction of S_μ, X, was calculated to be 0.096 as that at 442.8 K: S_μ reaches the maximum degree of polymerization at this temperature.[12]

Accordingly, the standard enthalpy of the formation of heptathiazocine, $\Delta H_f(S_7NH,s,298.15\ K)$, was estimated to be $89._3\pm1._1$ kJ mol^{-1}, assuming that the formation of S_π was negligible.

Discussion

Pyrolytic Processes of Heptathiazocine. The heptathiazocine finally decomposed into sulfur, nitrogen, and ammonia above 383 K in the argon atmosphere through the tetrasulfur tetranitride and tetrasulfur dinitride as the intermediates. Hydrogen sulfide was undetectable as a gaseous pyrolytic product in this work, whereas Becke-Goehring[2] has reported its formation in vacuo. The thermal degradation of 1,3,5,7,2,4,6,8-tetrathiatetrazocine (tetrasulfur tetraimide, $S_4(NH)_4$), also took place step by step without the formation of hydrogen sulfide in the argon atmosphere.[6] The primary pyrolytic reaction of this compound can be expressed as[6]

$$S_4(NH)_4 = 1/6\,S_8 + 2/3\,S_4N_4 + 4/3\,NH_3. \qquad (3)$$

According to these facts, the heptathiazocine may also release all the hydrogen atoms as in the form of ammonia during the first step of pyrolysis above 383 K in the argon atmosphere as

$$S_7NH = 19/24\,S_8 + 1/6\,S_4N_4 + 1/3\,NH_3. \qquad (4)$$

The tetrasulfur tetraimide yielded a fairly large amount, $n(S_4N_4)/n(S_4(NH)_4)=0.43$, of the tetrasulfur tetranitride at 383 K for 1.5 h in an argon atmosphere, in addition to the tetrasulfur dinitride which was produced by a secondary degradation of tetrasulfur tetranitride in the presence of sulfur.[6] On the other hand, the heptathiazocine gave only small quantities of tetrasulfur tetranitride and tetrasulfur dinitride, $n(S_4N_4)/n(S_7NH)=0.02$ and $n(S_4N_2)/n(S_7NH)<0.01$ respectively, during pyrolysis under the same conditions.

The decomposition of tetrasulfur tetranitride can be promoted in the presence of sulfur as:[6]

$$S_4N_4 = S_4N_2 + N_2(\text{in the presence of sulfur}) \qquad (5)$$

$$S_4N_2 = 1/2\,S_8 + N_2. \qquad (6)$$

The decomposition degree of tetrasulfur tetranitride was examined in the presence of different amounts of sulfur using two kinds of sulfur-mixed samples. The compositions of the sample were specified as $n(S_8)/n(S_4N_4)=0.25$ and 4.0, where n refers to the initial number of moles (these molar ratios correspond approximately to those expressed in Eqs. 3 and 4 respectively). Figure 3 shows the decomposition degree, α, of the tetrasulfur tetranitride as a function of heating time at 413 K in the closed system ($\approx$10 cm^3). The tetrasulfur tetranitride degraded slowly in the presence of a small amount of sulfur. On the other hand, the sulfur-rich sample was pyrolyzed much faster than the former sample through a pseudo first-order reaction. As clearly shown in Eq. 4, a large amount of sulfur is produced during primary pyrolysis; thus, the overall degradation of heptathiazocine would be greatly promoted. Thus, only small amounts of tetrasulfur tetranitride and tetrasulfur dinitride would be observed during the pyrolysis of heptathiazocine, in contrast to that of tetrasulfur tetraimide.

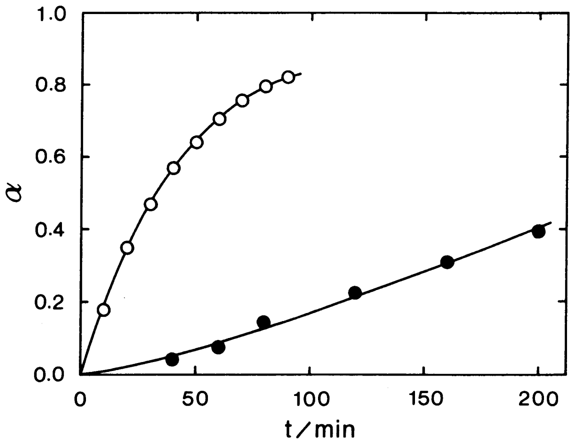

Fig. 3. Change in degradation degree of S_4N_4 in the presence of sulfur at 413 K in the closed system. Symbols: ○; $n(S_8)/n(S_4N_4)=4.0$ ●; $n(S_8)/n(S_4N_4)=0.25$.

Calculation of Standard Enthalpy of the Formation of Heptathiazocine. The heptathiazocine molecule consists of an eight-membered heterocyclic ring structure.[13] Its standard enthalpy of the formation can be deduced on the basis of the S–S, S–N, and N–H bond energies in the molecule and the standard enthalpies of the formation of atomic sulfur, nitrogen, and hydrogen, in addition to the enthalpy change of the sublimation of heptathiazocine. The standard enthalpies of the formation of these atomic species have been estimated as 277.4, 427.7, and 218.0 kJ mol^{-1},[14] respectively. The Sanderson method[15] gave the S–S, S–N, and N–H bond energies in the heptathiazocine molecule as 263, 245, and 363 kJ mol^{-1} based on their respective bond lengths.[13,16] Thus, the enthalpy of the formation of gaseous heptathiazocine, $\Delta H_f(S_7NH,g, 298.15 K)$, was calculated to be 200 kJ mol^{-1} using the above values.

The solubility parameter, δ, and molar volume, V, of heptathiazocine have been reported to be 26.0 J$^{1/2}$ cm$^{3/2}$ and 127 cm^3 mol^{-1}, respectively.[1] The former term is defined as $(E_v/V)^{1/2}$, where E_v is the vaporization energy; thus, the enthalpy change of the vaporization, ΔH_v, of heptathiazocine can be estimated as 88.2 kJ mol^{-1} by

$$\Delta H_V = \delta^2 V + RT. \tag{7}$$

The enthalpy change of the fusion of this compound was obtained as 18.8±0.6 kJ mol^{-1} (Table 3). Thus, the enthalpy change of the sublimation is estimated to be 107 kJ mol^{-1}.

On the other hand, the enthalpy change of the sublimation was also deduced from the London dispersion force, calculated by means of the Slater-Kirkwood equation as described in the previous paper.[7] The interatomic distances were calculated on the basis of the coordinates of atoms in the crystal lattice[13] assuming the N–H bond length to be 108 pm.[16] The enthalpy change of the sublimation was estimated as 109.0 kJ mol^{-1} taking into account 123 interatomic distances less than 500 pm.

The standard enthalpies of the formation of heptathiazocine were estimated as 93 and 91 kJ mol^{-1} by combining the enthalpy of the formation of gaseous state (200 kJ mol^{-1}) with the enthalpy changes of the sublimation (107 and 109 kJ mol^{-1}). The value, thus calculated, were close to the experimental value determined in this work (89.3±1.1 kJ mol^{-1}). Consequently, the standard enthalpy of the formation of heptathiazocine, $\Delta H_f(S_7NH,s,298.15 K)$, obtained by the DSC measurement, is considered reasonable.

References

1) S. Hamada, Y. Kudo, and M. Kawano, *Bull. Chem. Soc. Jpn.*, **48**, 2963 (1975).

2) M. Becke-Goehring, "Advanced in Inorganic Chemistry and Radiochemistry," Vol. 2, (1960), p. 159.

3) M. S. Shahid, H. G. Heal, and H. Garcia-Fernandez, *J. Inorg. Nucl. Chem.*, **33**, 4364 (1971).

4) M. Becke-Goehring and R. Schwarz, *Z. Anorg. Allg. Chem.*, **296**, 3 (1958).

5) H. G. Heal and J. Kane, "Inorganic Syntheses," ed by L. R. Morss, J. Merbaum, and W. L. Jolly, McGraw-Hill, New York (1968), Vol. XI, p. 184.

6) S. Hamada and Y. Kudo, *Bull. Chem. Soc. Jpn.*, **52**, 1063 (1979).

7) Y. Kudo and S. Hamada, *Bull. Chem. Soc. Jpn.*, **59**, 1257 (1986).

8) Y. Kudo and S. Hamada, *Bull. Chem. Soc. Jpn.*, **56**, 2627 (1983).

9) It is assumed that sulfur produced in this process exists as cyclooctasulfur, S_8.

10) The thermodynamic quantities of sulfur are expressed as S_8 units.

11) "JANAF Thermochemical Tables," 2nd ed., Nat. Bur. Stand. (US), (1971).

12) A. V. Tobolsky and A. Eisenberg, *J. Am. Chem. Soc.*, **81**, 780 (1959).

13) H. J. Hecht, R. Reinhardt, R. Steudel, and H. Bradaczek, *Z. Anorg. Allg. Chem.*, **426**, 43 (1976).

14) M. W. Chase, Jr., J. L. Curnutt, J. R. Downey, Jr., R. A. McDonald, A. N. Syverud, and E. A Valenzuela, *J. Phys. Chem. Ref. Data*, **11**, 840 (1982).

15) R. T. Sanderson, *J. Inorg. Nucl. Chem.*, **28**, 1553 (1966).

16) The N–H bond length was taken as the same as that in the tetrasulfur tetraimide molecule. See, T. M. Sabine and G. W. Cox, *Acta Crystallogr.*, **23**, 574 (1967).