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The Pyrolysis of 1,2,3,4,6,7-Hexathia-5,8-diazocine

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Crystals of 1,2,3,4,6,7-hexathia-5,8-diazocine (1,4-$S_6(NH)_2$) were transformed around 363 K with a molar enthalpy change of the transformation of 2.40±0.07 kJ mol^{-1}. Crystal systems of the two forms of 1,4-$S_6(NH)_2$ were identified to be orthorhombic (α-form) and monoclinic (β-form) below and above this temperature. Molar heat capacities of the α- and β-forms were also deduced as being 0.195±0.001 and 0.199±0.001 kJ mol^{-1} K^{-1} at 298.15 K, respectively. The 1,4-$S_6(NH)_2$ was pyrolyzed around its apparent melting point (405 K), producing tetrasulfur tetranitride (S_4N_4) and tetrasulfur dinitride (S_4N_2) as solid intermediates, which finally decomposed into sulfur, nitrogen, and ammonia under an argon atmosphere. A stoichiometric correlation among the final products gave an overall pyrolytic equation: 1,4-$S_6(NH)_2=3/4S_8+2/3N_2+2/3NH_3$. The standard enthalpy of the formation of α-form 1,4-$S_6(NH)_2$ was estimated as being 158±2 kJ mol^{-1} according to the observed enthalpy changes of the pyrolysis and transformation, which reasonably agreed with that calculated.

Hexathiadiazocine (hexasulfur diimide, $S_6(NH)_2$) is an eight-membered, puckered-type ring compound which resembles cyclooctasulfur, though two sulfur atoms are replaced by NH groups at 1,3-, 1,4-, and 1,5-positions, respectively. The crystal system of the 1,4-isomer has been reported to be monoclinic,[1] in contrast to those of the other two isomers, orthorhombic.[2,3] These geometric isomers are not so stable against daylight, even at room temperature, and thermally decompose around their respective melting points.[4—6]

Little information on the thermal decomposition has been available because of their instabilities and quite low yields upon syntheses.[4—6] In this work, one of the isomers, 1,2,3,4,6,7-hexathia-5,8-diazocine (1,4-$S_6(NH)_2$), was pyrolyzed in a temperature range from 320 to 513 K under an argon atmosphere to study its degradation process and thermodynamic property. The term 1,4-hexathiadiazocine hereafter refers to this 1,4-isomer.

Experimental

Materials. The 1,4-hexathiadiazocine was prepared by a method described by Heal and Kane.[6] A crude product was extracted from a reaction mixture with diethyl ether; the isomers were then respectively isolated from by-products by column chromatography, followed by repeated recrystallization from a carbon tetrachloride solution below 313 K. Thin-layer chromatography (TLC) showed that white needle crystals, thus obtained, were sufficiently pure to use in this work.[7]

Procedures. Pyrolytic products of the 1,4-hexathiadiazocine were identified by TLC and gas chromatography. Stoichiometric correlations among the final products were estimated in the same way as that described in previous papers,[8—10] as follows: a sample (33—160 mg) was heat-treated at 433 K for 90 min in an argon flow (25 cm^3 min^{-1}). Ammonia, one of gaseous products, was introduced into a perchloric acid solution and then titrated with a sodium hydroxide solution. The amount of nitrogen was also determined using an azotometer. Solid products were determined spectrophotometrically using their carbon tetrachloride solution.[9] The enthalpy changes of the transformation and thermal decomposition of 1,4-hexathiadiazocine, as well as its molar heat capacities, were estimated at heating rates of 8 and 16 K min^{-1} with a Perkin-Elmer (model DSC-1B) differential scanning calorimeter (DSC). The 1,4-hexathiadiazocine was carefully weighed and tightly sealed in an aluminium container (25 mm^3) under red light and the argon atmosphere. The DSC instrument was calibrated with indium of 99.999% purity. Sapphire of 99.998% purity was also used as a reference for measurements of the molar heat capacities of 1,4-hexathiadiazocine.

Differential thermal analysis (DTA) and thermal gravimetry (TG) on hexathiadiazocines were also carried out under an argon atmosphere using a thermal analyzer (Shimadzu, model DT-40). X-Ray powder diffraction patterns of 1,4-hexathiadiazocine were obtained with a Rigaku Denki Geigerflex (model RAD III A) X-ray diffractometer, the diffraction angles being calibrated using silicon.

Results

Pyrolytic Products and Degradation Process of 1,4-Hexathiadiazocine. The sample was heated in a DSC instrument at a heating rate of 16 K min^{-1} up to the specified temperatures. The solid pyrolytic products were identified by TLC after dissolving them in carbon tetrachloride, as shown in Table 1. Tetrasulfur tetranitride (S_4N_4) and tetrasulfur dinitride (S_4N_2) were

Table 1. Solid Pyrolytic Products of 1,4-$S_6(NH)_2$ at Different Temperatures[a]

T/K	Species			
403	$S_6(NH)_2$			
411	$S_6(NH)_2$	S_8[b]		
423	$S_6(NH)_2$	S_8	S_4N_4	S_4N_2[b]
433	$S_6(NH)_2$[b]	S_8	S_4N_4	S_4N_2[b]
443		S_8	S_4N_4	S_4N_2[b]
453		S_8	S_4N_4	S_4N_2[b]
463		S_8	S_4N_4[b]	
473		S_8		

a) Heating rate of 16 K min^{-1}. b) Trace amount.

observable as intermediates above 423 K under these conditions, whereas these two nitrides completely decomposed into sulfur and nitrogen[9] above 473 K. Thus, the solid final pyrolytic product of 1,4-hexathiadiazocine was only sulfur. The apparent decomposition temperature depended on both the heating rate and/or the duration of heating; for example, the 1,4-hexathiadiazocine obviously decomposed by prolonged heating, even at 383 K in an argon atmosphere. The fractional decomposition increased from 0.03 to 0.85 as the heating duration was extended from 90 to 180 min at this temperature.

Figure 1 shows a differential scanning calorimetric (DSC) pattern of the 1,4-hexathiadiazocine at a heating rate of 16 K min^{-1} in an argon atmosphere. The DSC curve showed a sharp endothermic peak attributable to fusion at 405 K[4] and a broad exothermic peak (430 K) with a shoulder. In addition, a small endothermic peak was indicated at 363 K. The 1,4-hexathiadiazocine heated above this temperature (393 K) indicated a quite different X-ray powder diffraction pattern compared with that of the original sample. Furthermore, the sample, thus preheated, no longer indicated such an endothermic peak at the DSC measurement, even if it was kept at room temperature for 50 days. However, the endothermic peak was once again observable when the preheated sample had been recrystallized from the carbon tetrachloride solution. According to these results, it can be concluded that the crystals of 1,4-hexathiadiazocine were transformed around 363 K, whereas its back-transformation took place very slowly. Thus, the original form will hereafter be expressed as an α-form and the other, as a β-form.

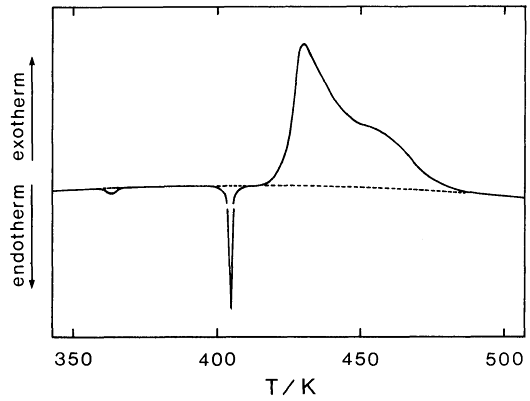

Fig. 1. DSC pattern of 1,4-hexathiadiazocine obtained at heating rate of 16 K min^{-1}.

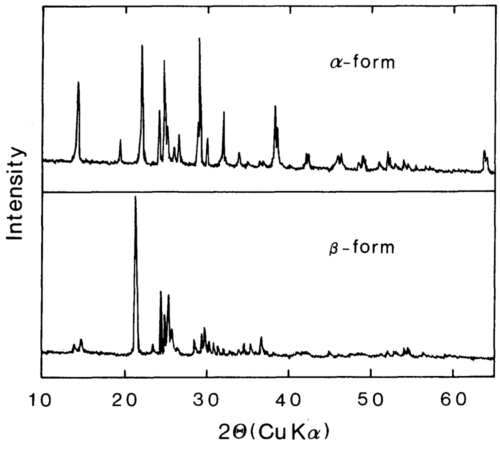

Fig. 2. X-Ray powder diffraction patterns of 1,4-hexathiadiazocines.

Stoichiometry of Pyrolytic Products during Thermal Degradation of 1,4-Hexathiadiazocine. Table 2 displays molar ratios of the pyrolytic products to the original 1,4-hexathiadiazocine upon heating at 433 K for 90 min. Trace amounts of tetrasulfur tetranitride and tetrasulfur dinitride were still detectable as $n(S_4N_4)/n(S_6(NH)_2)=3\times10^{-2}$ and $n(S_4N_2)/n(S_6(NH)_2)<5\times10^{-3}$, respectively. These two compounds, however, finally decomposed into sulfur and nitrogen.[9] Thus, the amounts of tetrasulfur tetranitride and tetrasulfur dinitride were converted to those of sulfur and nitrogen, respectively. The initial amount of the original sample did not affect these molar ratios under the same conditions. Based on these observations, the stoichiometric correlation during the overall pyrolysis of 1,4-hexathiadiazocine can be expressed as

$$1,4\text{-}S_6(NH)_2 = 3/4S_8 + 2/3N_2 + 2/3NH_3. \qquad (1)$$

Molar Heat Capacity of 1,4-Hexathiadiazocine. The molar heat capacities of 1,4-hexathiadiazocine, C_p, were estimated at a heating rate of 8 K min^{-1} between 320 and 393 K. The sample did not show any chemical change, except for transformation, after heating for 5 min at 393 K. Especially, C_p of the α-form 1,4-hexathiadiazocine was measured up to a temperature of 336 K, low enough to secure no transformation. Figure 3 shows the molar heat capacities of the two forms of 1,4-hexathiadiazocine as

Table 2. Molar Ratios of Final Pyrolytic Products of 1,4-$S_6(NH)_2$ at 433 K for 90 min

$n(S_6(NH)_2)$	Molar ratios of pyrolytic products		
	$\frac{n(S_8)}{n(S_6(NH)_2)}$	$\frac{n(N_2)}{n(S_6(NH)_2)}$	$\frac{n(NH_3)}{n(S_6(NH)_2)}$
μmol			
633	0.750	—	0.631
717	0.741	—	0.640
718	0.747	—	0.645
477	0.753	0.656	—
148	0.751	0.664	—
165	0.742	0.667	—
Average[a]	0.747±0.006	0.662±0.008	0.639±0.010

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

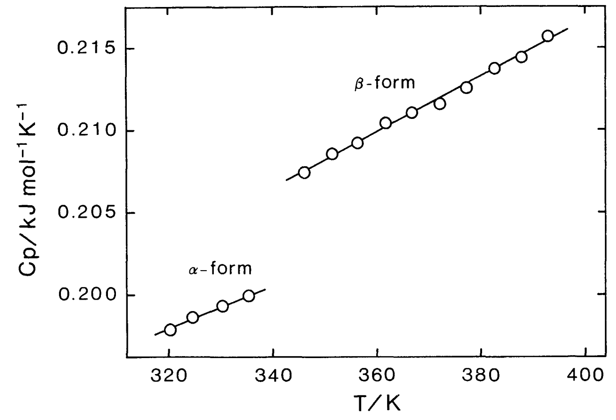

Fig. 3. Molar heat capacities of 1,4-hexathiadiazocines as a function of temperature.

a function of temperature. The molar heat capacities of α- and β-forms were deduced as 0.195±0.001 and 0.199±0.001 kJ mol^{-1} K^{-1} at 298.15 K, respectively, from linear relationships in the given temperature ranges, C_p (α-form)=0.156+1.30×10^{-4} T and C_p (β-form)=0.148+1.71×10^{-4} T. The correlation coefficients of the above linearities for α- and β-forms were calculated as 0.997 and 0.993, respectively.

Enthalpy Change during Pyrolysis of 1,4-Hexathiadiazocine in Argon Atmosphere. The enthalpy change during the overall pyrolysis of 1,4-hexathiadiazocine was measured at a heating rate of 16 K min^{-1} over temperatures ranging from 320 to 513 K. An apparent heat of fusion at 405 K was estimated as being 18.5±0.6 kJ mol^{-1}, though it would partially involve an enthalpy change of overlapped decomposition. On the other hand, an apparent enthalpy change of exothermic reaction around 430 K was obtained as −191±2 kJ mol^{-1}. Thus, the overall enthalpy change, ΔH, of the thermal decomposition starting from the β-form 1,4-hexathiadiazocine was estimated to be −173±2 kJ mol^{-1} as an average value (Table 3). The enthalpy change of the transformation of 1,4-hexathiadiazocine, ΔH_t(1,4-$S_6(NH)_2$), was separetely determined as being 2.40±0.07 kJ mol^{-1}, using a moderately large amount of the sample (Table 3). On the basis of the stoichiometric correlation (Eq. 1), the standard enthalpy of the formation of α-form 1,4-hexathiadiazocine, ΔH_f(1,4-$S_6(NH)_2$(α), s, 298.15 K), can be obtained as

$$\begin{aligned}&\Delta H_f(1,4\text{-}S_6(NH)_2(\alpha),\ s,\ 298.15\ K)\\&= -\Delta H - \Delta H_t(1,4\text{-}S_6(NH)_2) + 4/3RT + 3/4(\Delta H_t(\alpha,\beta)\\&\quad + \Delta H_m(\beta,\lambda) + X\Delta H_p) + 2/3\Delta H_f(NH_3,\ g,\ 298.15\ K)\\&\quad - \int_{298.15}^{T}\Delta C_p \mathrm{d}T, \qquad (2)\end{aligned}$$

where $\Delta H_t(\alpha,\beta)$ and $\Delta H_m(\beta,\lambda)$ are the enthalpy changes of the transformation of sulfur from S_α to S_β (3.2 kJ mol^{-1}) and of the fusion of S_β (13.8 kJ mol^{-1}),[11,12] ΔH_p the enthalpy change of the polymerization from S_λ to S_μ (13.3 kJ mol^{-1}),[11,13] and X the fraction of S_μ as the S_8 unit. The ΔH_f(NH_3, g, 298.15 K) is the standard enthalpy of the formation of ammonia (−45.9 kJ mol^{-1}),[12] and ΔC_p, the difference in the molar heat capacities between the α-form 1,4-hexathiadiazocine and the final pyrolytic products.[12,14] The reaction temperature, T, was taken as 430 K at the maximum of the broad exothermic peak, as shown in Fig. 1. The fraction of S_μ, X, was approximately evaluated to be 0.096 as that at the maximum degree of polymerization (442.8 K),[10,15] because the peak temperature (430 K) of the thermal decomposition was just below the polymerization temperature (432 K)[15] of S_λ. The integral term was calculated as being −0.65 kJ mol^{-1}. According to Eq. 2, the standard enthalpy of the formation of α-form 1,4-hexathiadiazocine, ΔH_f (1,4-$S_6(NH)_2$(α), s, 298.15 K), was estimated to be 158±2 kJ mol^{-1}.

Table 3. Enthalpy Changes of Decomposition and Transformation of 1,4-$S_6(NH)_2$

$n(S_6(NH)_2)$	ΔH[a]	$n(S_6(NH)_2)$	ΔH_t(1,4-$S_6(NH)_2$)
μmol	kJ mol^{-1}	μmol	kJ mol^{-1}
3.47	−175	32.87	2.46
2.29	−172	34.23	2.45
3.27	−175	30.89	2.48
3.20	−174	32.53	2.37
3.47	−168	39.55	2.37
2.96	−175	41.45	2.36
3.10	−174	30.72	2.28
3.43	−171	Average	2.40±0.07
3.07	−170		
2.94	−176		
2.92	−170		
3.25	−177		
Average[b]	−173±2		

a) The enthalpy change involves the heat of fusion. b) The uncertainty value was estimated in the same manner in Table 2.

Discussion

Transformation of Hexathiadiazocine Crystal. The 1,4-hexathiadiazocine was transformed around 363 K, whereas the 1,3- and 1,5-hexathiadiazocines did not show any endothermic peak attributable to the transformation. The enthalpy change of the transformation of the former compound (2.40±0.07 kJ mol^{-1}) was smaller than that of sulfur (3.2 kJ mol^{-1}) from orthorhombic (S_α) to monoclinic system (S_β).[11,12] The β-form 1,4-hexathiadiazocine was assigned to a monoclinic system, because observed spacings on X-ray powder diffractometry were in good agreement with those calculated according to the crystallographic parameters (a_0=805.4, b_0=1252.2, c_0=836.8 pm, and β=114.45°).[1]

The unit cell lengths and Miller indices for X-ray powder diffraction peaks of the α-form 1,4-hexathiadiazocine were deduced according to the Lipson's method,[16] assuming the crystal system to be orthorhombic like those of sulfur(α) and other family compounds of sulfur imides, as shown in Table 4. As pointed out by Lipson, particular pinacoidals, Q_{h00}, Q_{0k0}, and Q_{00l}, would be frequently found among a number of differences between respective couples of observed pinacoidals, Q_{hkl}, for the thirty seven X-ray powder diffraction peaks in a Cu*K*α 2Θ range from 10 to 70°; here, Q_{hkl} stands for the reciprocal of the squared spacing, $1/d_{hkl}^2$. Since the Q_{h00}, Q_{0k0}, and Q_{00l}, thus obtained, equal $(h_1^2-h_2^2)Q_{100}$, $(k_1^2-k_2^2)Q_{010}$, and $(l_1^2-l_2^2)Q_{001}$, respectively, the Q_{100}, Q_{010}, and Q_{001} would also be frequently observable among quotients, Q_{h00}/n, Q_{0k0}/n, and Q_{00l}/n, where n can be taken as 1, 3, 4, 5, 7, 8, 9, 12, 15, and 16, respectively. Thus, a computational treatment gave the unit cell lengths for α-form 1,4-hexathiadiazocine.

The number of molecules, Z, in the unit cell would be sixteen, compared with unit cell volumes of 1,3- and 1,5-hexathiadiazocines, as indicated in Table 4. According to these results, the Miller indices were assigned for all of the observed diffraction peaks (Table 5) with repeated refinements of the unit cell lengths, taking into account possible reflections.[20] The values of unit cell lengths, $a_0=1623$, $b_0=1246$, and $c_0=1428$ pm, in Table 4 were thus obtained. However, diffraction peaks less than 175 pm of the spacing were omitted in Table 5, since the assignment of the Miller indices was uncertain at high diffraction angles (as usual), though the observed spacings closely agreed with those calculated.

It was difficult to confirm the space group of α-form 1,4-hexathiadiazocine from X-ray powder diffractometry, because the diffraction pattern was attributable to both space groups, D_{2h}^{25}-*Immm* and D_{2h}^{28}-*Imma*. The density of α-form 1,4-hexathiadiazocine was calculated to be 2.05 g cm^{-3}, which reasonably agreed with that observed (2.00 g cm^{-3}).[1]

Pyrolytic Process of 1,4-Hexathiadiazocine. The 1,4-hexathiadiazocine finally decomposed into sulfur, nitrogen, and ammonia through tetrasulfur tetranitride and tetrasulfur dinitride as intermediates. In order to compare the thermal decomposition of three

Table 4. Crystallographic Parameters of Sulfur and Sulfur Imides

Compound	Unit cell lengths			Angle β/°	Z[a]	Crystal system	Ref.
	a_0/pm	b_0/pm	c_0/pm				
S_8 (α)	1046.5	1286.6	2448.6		16	O[b]	17
S_8 (β)	1090	1096	1102	83.27	8	M[c]	17
S_7NH	761	804	1303		4	O	18
1,3-$S_6(NH)_2$	817.1	1281.5	1403.5		8	O	2
1,4-$S_6(NH)_2$ (α)	1623	1246	1428		16	O	This work
1,4-$S_6(NH)_2$ (β)	805.4	1252.2	836.8	114.45	4	M	1
1,5-$S_6(NH)_2$	738.6	786.4	1282.8		4	O	3
$S_4(NH)_4$	801.0	1220.0	672.7		4	O	19

a) The number of molecules in the unit cell. b) Orthorhombic. c) Monoclinic.

Table 5. Spacings and Miller Indices of α-Form 1,4-$S_6(NH)_2$

No.	Observed		Calculated		No.	Observed		Calculated	
	d/pm	I/I_0[a]	d/pm	*hkl*		d/pm	I/I_0	d/pm	*hkl*
1	622	0.65	623	020[b]	14	257	0.06	257	143
2	457	0.19	457	103	15	247	0.05	247	440
3	405	0.96	406	222,400				246	523
4	369	0.45	370	230	16	243	0.06	242	334
			368	123	17	235	0.47	235	044
5	358	0.84	359	032	18	234	0.31	234	325,622
			358	231	19	215	0.13	215	316
6	356	0.28	357	004,303				214	226,505
7	341	0.13	340	420	20	198	0.09	198	723,(550)[c]
8	336	0.24	336	114	21	197	0.12	196	605
9	310	0.36	311	040	22	188	0.06	188	055
			310	024,323	23	186	0.13	186	822,(740)
10	308	1.00	309	403	24	178	0.07	179	(910)
			307	422				178	008
11	298	0.24	298	304	25	175	0.17	175	264
12	280	0.44	281	105					
13	265	0.06	265	341	plus 12 diffraction peaks				

a) Relative intensity. b) The unparenthesized Miller indices are assignable for both the space groups D_{2h}^{25} and D_{2h}^{28}. c) The Miller indices in parentheses can be additionally assigned as the space group D_{2h}^{25}.

isomers, differential thermal analysis and thermal gravimetry on 1,3-, 1,4-, and 1,5-hexathiadiazocines were carried out at a heating rate of 5 K min^{-1} in an argon flow, as shown in Fig. 4. A broad exothermic peak with a shoulder demonstrated a step-by-step decomposition of 1,3- and 1,4-hexathiadiazocines. A two-step weight loss on the TG curves up to 450 K also supported the above-mentioned step-by-step decomposition process. The DTA and TG patterns of 1,3- and 1,4-isomers were similar to those of 1,3,5,7-tetrathia-2,4,6,8-tetrazocine (tetrasulfur tetraimide, $S_4(NH)_4$)[21] and heptathiazocine (heptasulfur imide, S_7NH).[10] On the other hand, the 1,5-hexathiadiazocine indicated an apparent melting point of 429 K higher than those of the 1,3- and 1,4-isomers (403 and 404 K, respectively), and then thermally decomposed. Tetrasulfur tetranitride as the intermediate degrades into sulfur and nitrogen around 430 K in the presence of sulfur.[9] Thus, an overlapped decomposition of the first and second steps took place, which did not show any shoulder of the exothermic peak on DTA. Primary pyrolytic reactions of heptathiazocine and tetrathiatetrazocine were expressed as follows:[10,21]

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

and

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

Shahid et al.[22] have mentioned that a rather large amount of tetrasulfur tetranitride was yielded during the decompositions of three isomers of hexathiadiazocine at 413—433 K. According to these facts and the results given in Table 1, a primary reaction of 1,4-hexathiadiazocine, as well as 1,3- and 1,5-hexathiadiazocines, can be proposed as

$$1,4\text{-}S_6(NH)_2 = 7/12S_8 + 1/3S_4N_4 + 2/3NH_3, \qquad (5)$$

followed by a secondary decomposition of tetrasulfur tetranitride in the presence of sulfur.[9]

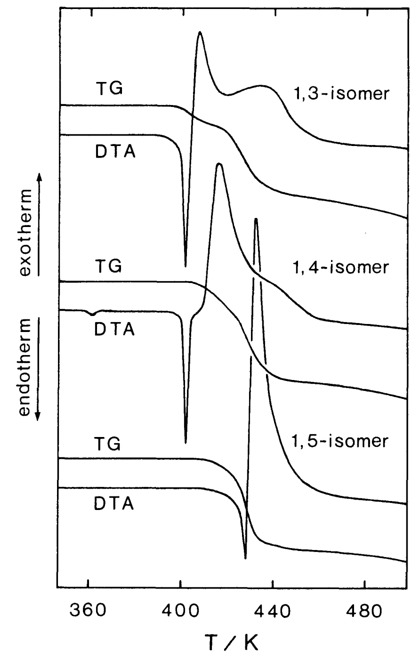

Fig. 4. DTA and TG patterns of 1,3-, 1,4-, and 1,5-isomers observed under argon atmosphere.

Calculation of Standard Enthalpy of the Formation of α-Form 1,4-Hexathiadiazocine. The bond energies in the 1,4-hexathiadiazocine molecule can be calculated by the Sanderson's method[23] based on their respective bond lengths[1] and electronegativities. The standard enthalpy of the formation of gaseous 1,4-hexathiadiazocine was calculated as 249 kJ mol^{-1} from the bond energies of S–S, S–N, and N–H, thus calculated,[24] and the standard enthalpies of the formation of atomic sulfur, nitrogen, and hydrogen.[12]

The enthalpy change of the sublimation was also calculated from the London dispersion force by the Slater–Kirkwood equation, as described in previous papers.[10,21] The enthalpy change of the sublimation of β-form 1,4-hexathiadiazocine was estimated to be 92 kJ mol^{-1}, taking into account 150 interatomic distances less than 500 pm, based on the atomic configuration in the β-type crystal structure.[1] The standard enthalpy of the formation of α-form 1,2,3,4,6,7-hexathia-5,8-diazocine, therefore, was estimated as being 155 kJ mol^{-1} by combining the enthalpy of the formation of the gaseous state (249 kJ mol^{-1}) with enthalpy changes of the sublimation (β-form, 92 kJ mol^{-1}) and of the transformation (2.40±0.07 kJ mol^{-1}). This value was close to the observed one (158±2 kJ mol^{-1}).

The standard enthalpies of the formation of heptathiazocine and tetrathiatetrazocine have been estimated as being 89±1 and 318±7 kJ mol^{-1}, respec-

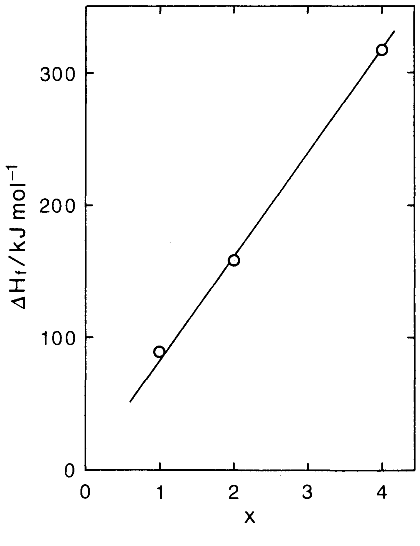

Fig. 5. Standard enthalpies of formation of sulfur imide compounds, $S_{8-x}(NH)_x$, as a function of number of NH groups.

tively.[10,21] Thus, the standard enthalpies of the formation of a series of cyclic sulfur imide compounds, $S_{8-x}(NH)_x$ (x=1, 2, and 4), increased linearly with an increase in the NH groups in their molecules, as shown in Fig. 5.

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