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Pyrolysis of Tetrasulfur Tetraimide

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Tetrasulfur tetraimide was pyrolyzed into sulfur, tetrasulfur tetranitride, tetrasulfur dinitride, ammonia, and nitrogen even below its apparent melting point, 143 °C, under atmospheric pressure; a small amount of heptasulfur imide was also observable. The tetrasulfur dinitride and nitrogen were formed from subsequent reactions between products. The overall pyrolysis consisted of the primary decomposition and the following subsequent ones, as judged from the stoichiometric relationships among the pyrolytic products: $3S_4(NH)_4 = 4S + 2S_4N_4 + 4NH_3$, $S_4N_4 = S_4N_2 + N_2$ (in the presence of sulfur), and $S_4N_2 = 4S + N_2$. Partial pressures of ammonia at the primary pyrolysis were estimated to be 8.5×10^{-2}, 2.1×10^{-1}, 5.2×10^{-1}, and 1.4 Pa at 60, 70, 80, and 90 °C respectively.

Sasaki *et al.*[1] have reported that tetrasulfur tetraimide, $S_4(NH)_4$, melted at 152 °C with an accompanying decomposition on moderately rapid heating, while it was stable in air at room temperature. They have proposed that tetrasulfur tetraimide pyrolyzed as follows over the temperatures from 110 to 135 °C *in vacuo*:

$$3S_4(NH)_4 = 4S + 2S_4N_4 + 4NH_3$$

In this work, the pyrolysis of tetrasulfur tetraimide was studied under atmospheric pressure because there have been few investigations under these conditions.

Experimental

Materials. The tetrasulfur tetraimide was prepared by the method described by Meuwsen[2] as follows: the tetrasulfur tetranitride, S_4N_4,[3] was reduced by adding an ethanolic solution of tin(II) chloride into its benzene solution. A crude product was purified by repeated recrystallization from an acetone and a methanol solution. The tetrasulfur tetraimide thus obtained was confirmed to be pure enough to use in this work by thin-layer chromatography.

Procedures. A differential thermal analysis and a thermal gravimetry of the tetrasulfur tetraimide were carried out at the heating rate of 3 °C/min in an argon atmosphere with a Rigaku Denki Thermoflex, model 8002, differential thermal analyzer. Solid pyrolytic products of the tetrasulfur tetraimide were identified by the TLC as follows: a sample was heated in the argon flow up to the specified temperatures in the DTA equipment, and then was identified by using chlorobenzene, cyclohexane, and carbon tetrachloride as developing solvents. A silver nitrate solution was used as a detecting reagent after quenching. An infrared spectrum of the heat-treated sample was also taken to identify the pyrolytic products, using an IR spectrophotometer, model DS-403G, from the Japan Spectroscopic Co.

The sample was pyrolyzed to identify gaseous products and to estimate their amounts; a glass vessel with a small dead space was employed at the specified temperatures. The gaseous products were identified with a gas chromatograph, model 80, from the Yanagimoto Seisakusho. A silica gel column was used as a stationary phase and helium as a carrier gas. The amount of ammonia, one of the gaseous products, was estimated coulometrically[4,5] during the pyrolysis in the argon and carbon dioxide atmospheres. The amount of nitrogen, another one of the gaseous products, was estimated with an azotometer by using the carbon dioxide as the carrier gas, after removing the accompanying ammonia into diluted perchloric acid.

The partial pressure of ammonia during the pyrolysis was measured over the temperatures from 60 to 90 °C in the argon and the nitrogen atmospheres by a method of transpiration.[6,7] The specified temperature of the sample was kept within a precision of ±0.05 °C. The flow rate of the carrier gas was controlled automatically over the range from 77.4 to 125 cm^3/min. The total volume of the carrier gas was measured with a wet-type gas flowmeter, model WK-0.5, from the Shinagawa Seisakusho. The amount of ammonia in the carrier gas was estimated coulometrically after the gas flow was passed through an ice-cold trap to remove volatile solid products.

Results

The Solid Pyrolytic Products of Tetrasulfur Tetraimide. The solid pyrolytic products were identified to be sulfur, tetrasulfur tetranitride, tetrasulfur dinitride, S_4N_2, and heptasulfur imide, S_7NH, by the TLC, as shown in Table 1. Both the tetrasulfur tetranitride[8,9] and the tetrasulfur dinitride[10] were also confirmed by the IR spectrometry, though the heptasulfur imide was unde-

TABLE 1. RESULTS OF TLC ON SOLID PYROLYTIC PRODUCTS OF TETRASULFUR TETRAIMIDE

Solvent	R_f value				
	S_8	S_4N_4	S_4N_2	S_7NH	$S_4(NH)_4$
Chlorobenzene	1.0 (1.0)[a]	0.61 (0.61)		0.88 (0.88)	0.15 (0.15)
Carbon tetrachloride	0.92 (0.92)	0.47 (0.42)		0.70 (0.68)	0.0 (0.0)
Cyclohexane	0.80 (0.82)	0.16 (0.14)	0.66 (0.67)	0.35 (0.36)	0.0 (0.0)

a) The R_f values in parentheses were previously determined for each species.

TABLE 2. SOLID PYROLYTIC PRODUCTS AT EACH TEMPERATURE

t/°C	Species				
90	$S_4(NH)_4$				
100	$S_4(NH)_4$	S_8			
110	$S_4(NH)_4$	S_8	S_4N_4		(S_7NH)[a]
120	$S_4(NH)_4$	S_8	S_4N_4	S_4N_2	(S_7NH)
130	$S_4(NH)_4$	S_8	S_4N_4	S_4N_2	(S_7NH)
140	$S_4(NH)_4$	S_8	S_4N_4	S_4N_2	(S_7NH)
150	$S_4(NH)_4$	S_8	S_4N_4	S_4N_2	(S_7NH)
160		S_8	S_4N_4	S_4N_2	(S_7NH)
170		S_8	S_4N_4	S_4N_2	(S_7NH)
180		S_8			

a) Very small amount.

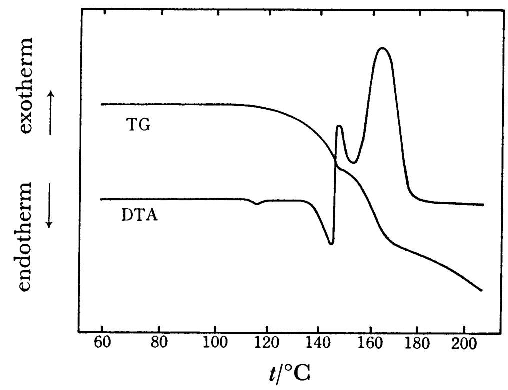

Fig. 1. DTA and TG patterns of tetrasulfur tetraimide.

tectable because of its small amount. The kinds of products at each temperature are shown in Table 2.

Figure 1 shows the DTA and the TG patterns of the tetrasulfur tetraimide taken in the argon atmosphere. An endothermic peak at 143 °C was confirmed to be caused by fusion of tetrasulfur tetraimide,[1] while the apparent melting point increased with increasing the heating rate, *e.g.*, 143, 149, and 152 °C at 3, 5, and 10 °C/min respectively. The tetrasulfur tetraimide was pyrolyzed even below its apparent melting point, judging from a weight loss in the TG and the results in Table 2. The tetrasulfur tetraimide disappeared at 160 °C under these conditions as is shown in Table 2, though it vanished even at 150 °C by heating for 1 h. The sample pre-heated at 150 °C showed only the exothermic peak at 165 °C, besides a small endothermic peak around 115 °C arising from the fusion of sulfur. Judging from these results, the exothermic peaks at 147 and 165 °C were attributable to a vigorous decomposition of tetrasulfur tetraimide and a subsequent decomposition of the pyrolytic products respectively: the contribution of heptasulfur imide to the DTA pattern was obscure because of its small amount.

The weight loss in the TG from about 105 to 147 °C was considered to originate mainly from the primary pyrolysis of the tetrasulfur tetraimide, which was accompanied by evolution of the gas and sublimation of the resulting tetrasulfur tetranitride.[7] The weight loss at the second stage above 147 °C was chiefly attributable to the subsequent decomposition of the pyrolytic products which accompanied the formation of the gas and was followed in turn by vaporization of molten sulfur. Judging from the weight loss, about 30 wt % at 140 °C, at the first stage and the kinds of the pyrolytic products, the subsequent decomposition was also expected to occur even below 147 °C.

Amounts of the tetrasulfur tetranitride and the sulfur in the sample heated at 110 °C for 1.5 h were estimated to be 0.431 and 1.69 respectively, as the molar ratios to the original tetrasulfur tetraimide. A spectrophotometric technique was used after separating the materials chromatographically by using a silica gel column. These values disagreed with those proposed by Sasaki *et al.*[1] The amount of the tetrasulfur dinitride could not be estimated because the tetrasulfur dinitride was easily hydrolyzed in the silica gel column, which contained about 6% water, during the chromatographic separation. Goehring *et al.*[11] have reported that tetrasulfur dinitride produced an equivalent amount of ammonia on its hydrolysis. Therefore, the amount of the tetrasulfur dinitride could be deduced to be 0.257 mol against 1 mol of tetrasulfur tetraimide from a mass balance of nitrogen. The amount of the heptasulfur imide was also estimated to be 0.027 as the molar ratio to the original material: the amount of hydrogen in the observed heptasulfur imide was less than 0.7 mol % against that in the original tetrasulfur tetraimide, so that the formation of heptasulfur imide could be neglected in this case.

The Gaseous Pyrolytic Products of Tetrasulfur Tetraimide. The gaseous products were identified to be ammonia and nitrogen by the gas chromatography on the pyrolysis at 120 °C for 2 h in the argon and the carbon dioxide atmospheres, while neither hydrogen nor hydrogen sulfide was observable. Both ammonia and nitrogen were also detected even at 80 °C in the same atmospheres.

The tetrasulfur tetraimide was pyrolyzed in order to estimate the amount of ammonia over the temperatures from 80 to 160 °C for 1.5—6 h in the argon and the carbon dioxide flows. The molar ratio of the ammonia to the original tetrasulfur tetraimide was estimated to be 1.33 ± 0.008 under these conditions; this value did not depend on the temperature or on the kinds of the carrier gases. Therefore, all the hydrogen atoms in tetrasulfur tetraimide were considered to be released in the form of ammonia by the pyrolysis, though a negligibly small part of the hydrogen was converted into the form of heptasulfur imide. The amount of the nitrogen was estimated with the azotometer over the temperatures from 80 to 170 °C in the carbon dioxide flow, after the accompanying ammonia was absorbed into diluted perchloric acid. Figure 2 shows the molar ratio of the produced nitrogen to the original tetrasulfur tetraimide against the temperature. The molar ratio increased linearly with increasing the temperature up to about 140 °C and then further increased with a steeper slope above 140 °C. This temperature nearly corresponded to the apparent melting point of tetrasulfur tetraimide, so that the increase in the formation of nitrogen above

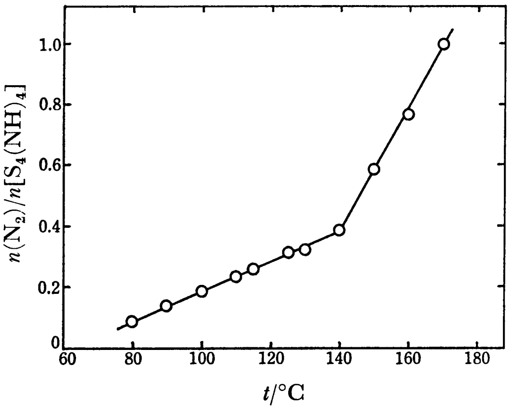

Fig. 2. Molar ratio of produced nitrogen to tetrasulfur tetraimide against temperature.

140 °C was considered to be due to the vigorous decomposition of tetrasulfur tetraimide after fusion and the subsequent decomposition of the pyrolytic products.

The Partial Pressure of Ammonia during the Pyrolysis. In order to estimate apparent partial pressures of ammonia by the method of transpiration,[6,7] the tetrasulfur tetraimide was homogeneously mixed with the tetrasulfur tetranitride to keep proper vapor pressures of tetrasulfur tetranitride at given temperatures[7] in the reaction vessel. A sufficient amount of the ammonia was directly absorbed into an electrolytic solution for the coulometric titration, *i.e.*, 6.5—37.0 μg. The total volume of the carrier gas ranged from 2.4 to 15.0 dm^3 (from 30 to 120 min) as the standard state. The apparent partial pressure, p, of the ammonia was calculated by the following equation, on the assumption that the law of partial pressure was obeyed: $p=nRT(P+p')/[nRT+(P+p''-p_w)V]$. Where P is the atmospheric pressure, p', the excess pressure in the reaction vessel, p'', the excess pressure in the gas flowmeter, p_w, the vapor pressure of water in the gas flowmeter, n, the number of moles of the ammonia, V, the volume of the carrier gas, and R, the gas constant.

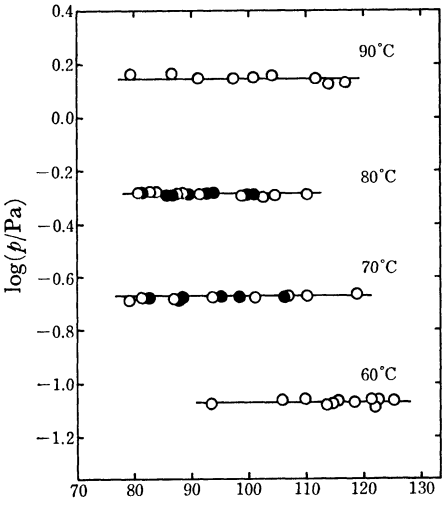

Fig. 3. Relationship between apparent partial pressure of ammonia and flow rate of carrier gas.
○: Estimated in Ar atmosphere, ●: estimated in N$_2$ atmosphere.

Figure 3 shows the relationship between the apparent partial pressure of the ammonia and the flow rate of the carrier gas. The values of the apparent partial pressures were almost equal at each temperature within these flow rate. Accordingly, it can be concluded that the formation of the ammonia in this system was in an equilibrium state. Therefore, the partial pressures of the ammonia during the pyrolysis were estimated to be 8.5×10^{-2}, 2.1×10^{-1}, 5.2×10^{-1}, and 1.4 Pa at 60, 70, 80, and 90 °C respectively; these are the averages of the apparent values estimated in the argon atmosphere (open circles). The apparent partial pressures estimated in the nitrogen atmosphere (closed circles) agreed with those estimated in the argon atmosphere at 70 and 80 °C, as is shown in Fig. 3. The partial pressures of the ammonia during the pyrolysis were not affected by the kinds of the carrier gases, *i.e.*, argon and nitrogen.

Discussion

The overall pyrolysis of tetrasulfur tetraimide under atmospheric pressure was not so simple as that reported by Sasaki *et al.*[1] All the hydrogen atoms in imide groups of tetrasulfur tetraimide were converted into those in the form of ammonia, judging from their stoichiometric relationship, while a very small part of the imide group remained in the form of heptasulfur imide. On the contrary, the nitrogen atoms were converted into not only the form of tetrasulfur tetranitride but also the forms of nitrogen and tetrasulfur dinitride during the pyrolysis, and a simple stoichiometric relationship could not be obtained among them.

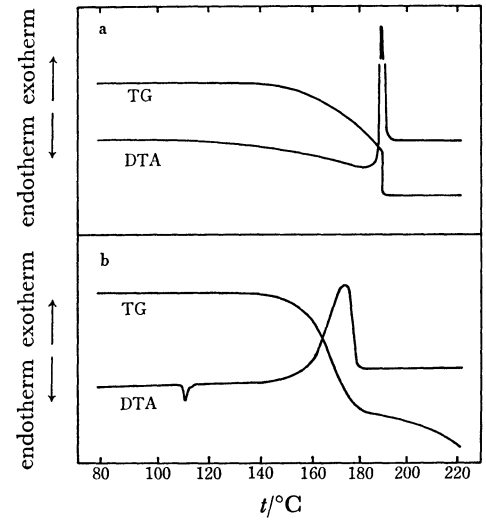

Fig. 4. DTA and TG patterns of tetrasulfur tetranitride
a: S$_4$N$_4$, b: S$_4$N$_4$+S$_8$ (molar ratio, 4: 1).

The tetrasulfur tetranitride showed a very sharp exothermic peak at 190 °C, along with an abrupt weight loss in the argon atmosphere on its DTA and TG, as is shown in Fig. 4a: it decomposed explosively into its elements at this temperature. No nitrogen could be detected below this temperature, though Goehring *et al.*[12] have reported that it decomposed above 130 °C. Heal[13] has described that tetrasulfur tetranitride decomposed gently above 120 °C when it was mixed with a large amount of sulfur. Figure 4b shows a DTA pattern of the tetrasulfur tetranitride mixed with the sulfur at the molar ratio of 4: 1 in the argon atmosphere. A broad exothermic peak was observed at 174 °C in the DTA instead of the sharp one at 190 °C for the pure tetrasulfur tetranitride, besides a small endothermic peak around 110 °C attributable to the fusion of sulfur. Furthermore, the exothermic peak temperature of the mixed sample decreased from 174 to 165 °C upon increasing the molar ratio of the sulfur from 4: 1 to 1: 4. Backens[14] has reported that tetrasulfur dinitride was produced by the gentle decomposition of tetrasulfur tetranitride mixed with sulfur above 125 °C. The tetrasulfur dinitride was observed on the pyrolysis of the tetrasulfur tetranitride mixed with the sulfur at 160 °C in the argon atmosphere. An evolution of nitrogen was also confirmed during the pyrolysis of the same sample even at 140 °C. Consequently, the pyrolysis of tetrasulfur tetranitride was concluded to be accelerated in the presence of sulfur. The exothermic peak at 165 °C in Fig. 1 was confirmed to be attributable to this reaction.

It can be concluded that the formations of tetrasulfur dinitride and nitrogen originate from the subsequent pyrolysis of the tetrasulfur tetranitride in the presence of the sulfur, followed by the decomposition of the tetrasulfur dinitride because of its instability,[15] as follows:

$$S_4N_4 = S_4N_2 + N_2 \text{ (in the presence of sulfur)}, \tag{1}$$

$$S_4N_2 = 4S + N_2. \tag{2}$$

This consideration can be supported by the fact that the apparent partial pressures of the ammonia during the pyrolysis were independent of the kinds of the carrier gases, *i.e.*, argon and nitrogen.

TABLE 3. MOLAR RATIOS OF PYROLYTIC PRODUCTS TO TETRASULFUR TETRAIMIDE AT 110 °C

	S	S_4N_4	NH_3	N_2	S_4N_2	S_7NH
Overall reaction	1.69	0.431	1.33	0.235	0.257[a]	0.027
Primary reaction	—[b]	0.666[c]	1.33			
Sasaki *et al.*[1]	1.33	0.667	1.33			

a) Deduced. b) Unestimated. c) Calculated.

The amount of the tetrasulfur tetranitride produced at the primary pyrolysis can be calculated from the estimated amounts of the species and Eqs. 1 and 2, as is shown in Table 3. The amount of the sulfur to be produced at the first stage, however, could not be deduced because of the complicated hydrolysis of tetrasulfur dinitride with respect to sulfur atoms.[11,16] The primary pyrolysis of tetrasulfur tetraimide is considered to be the same as that reported by Sasaki *et al.*,[1] judging from the results in Table 3 and the process of the pyrolysis:

$$3S_4(NH)_4 = 4S + 2S_4N_4 + 4NH_3. \tag{3}$$

The van't Hoff plots of the partial pressure of the ammonia showed a good linear relationship, while the value at 90 °C was overestimated to some degree because of the extra formation of ammonia arising from the reaction between a trace amount of tetrasulfur dinitride and water.[11]

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