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The Formation of Tetrasulfur Dinitride during the Mild Pyrolysis of Tetrasulfur Tetranitride

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Tetrasulfur dinitride was formed by the mild pyrolysis of tetrasulfur tetranitride in the presence of a large amount of sulfur. The stoichiometric correlations of the pyrolytic products indicated a step-by-step degradation of the tetrasulfur tetranitride. Differential scanning calorimetry of an interrupted pyrolysis and determinations of the products gave the enthalpy of the formation of gaseous tetrasulfur dinitride as 351±3 kJ mol^{-1}, which was reasonable judging from the bond enengies calculated by Sanderson's method and those deduced from known bond energies. The obtained standard enthalpy of the formation of tetrasulfur tetranitride was 469±1 kJ mol^{-1}, which agreed with the value reported by Barker *et al.*

Heal[1)] mentiond that tetrasulfur tetranitride, S_4N_4, decomposed slowly above 120 °C in the presence of a large amount of sulfur, whereas the pure crystals broke down explosively to sulfur and nitrogen upon heating at 190 °C.[1,2)] Backens[3)] pointed out that tetrasulfur dinitride, S_4N_2, appeared on the mild pyrolysis of tetrasulfur tetranitride mixed with sulfur above 125 °C. Little information on the pyrolysis of tetrasulfur dinitride is available because of its thermal instability.[1,4)] In this work, the formation of tetrasulfur dinitride during mild pyrolysis was studied quantitatively. Furthermore, the enthalpy of the formation of tetrasulfur dinitride was estimated and discussed.

Experimental

Materials. The tetrasulfur tetranitride was prepared using the method described by Jolly and Becke-Goehring[5)] as follows. Disulfur dichloride vapor was reacted with ammonium chloride pellets at 200 °C for 48 h. The crude product was purified by column chromatography and then recrystallized repeatedly from a benzene solution. Thin-layer chromatograph (TLC) analysis showed that the tetrasulfur tetranitride thus obtained was pure enough to be used in this work. The sulfur was recrystallized several times from a carbon disulfide solution. A homogeneous mixture of sulfur and tetrasulfur tetranitride powder was obtained by a thorough grinding of the compounds at molar ratios ranging from 0.20 to 0.80.

Procedures. Differential thermal analysis (DTA) and thermal gravimetry (TG) were carried out on samples heated at a rate of 3 °C min^{-1} in an argon atmosphere with a Rigaku Denki Thermoflex, model 8002, differential thermal analyzer.

The mixed sample (100—220 mg), placed in a reaction tube, was pyrolyzed at specified temperatures, which were kept constant to ±0.1 °C using a thermostated aluminium block. Volatile pyrolytic products were removed from the reaction tube by the use of a carbon dioxide carrier gas at a flow rate of 30 cm^3 min^{-1} and finally trapped at −30 °C. The trapped product and the solid that remained in the reaction tube were dissolved in small volumes of carbon tetrachloride and used for the identification and determination of the constituent species. The concentrations of tetrasulfur tetranitride, tetrasulfur dinitride, and sulfur in the solution were obtained from a spectrum over the wave-length region from 320 to 480 nm based on the corresponding molar absorption coefficients previously determined (Fig. 1). A freshly prepared pure tetrasulfur dinitride[6)] was used to determine its own spectrum. The amount of nitrogen resulting from the decomposition of tetrasulfur tetranitride was estimated with an azotometer after trapping the volatile products.

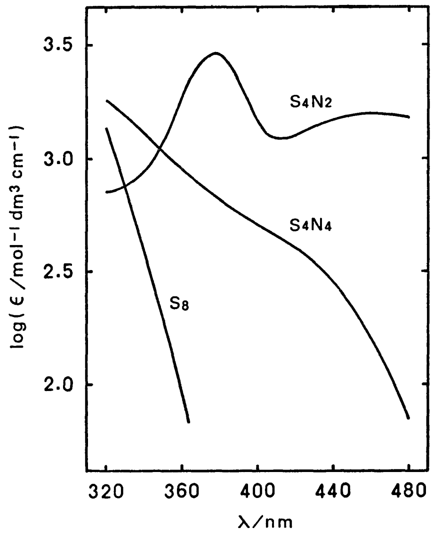

Fig. 1. Absorption spectra of S_4N_2, S_4N_4, and S_8 in CCl_4 solutions.

The heat of decomposition of the sample was measured with a Perkin-Elmer model DSC-1B differential scanning calorimeter at the heating rate of 4 °C min^{-1}. The sample was tightly sealed in an aluminium container under an argon atmosphere, and the equipment was calibrated with indium of a 99.999% purity under the same conditions.

Results

Differential Thermal Analysis of Tetrasulfur Tetranitride Mixd with Sulfur and Its Pyrolytic Products. The pure tetrasulfur tetranitride decomposed abruptly at 190 °C in the argon atmosphere, as is shown in Fig. 2a. The DTA of the mixed sample showed a broad exothermic peak in addition to the endothermic peaks resulting from the fusion of sulfur. The exothermic-peak temperature became lower as the sulfur content increased(Figs. 2b and 2c). The TG also indicated an enhanced decomposition of the mixed sample, while a decrease in the weight of the pure sample resulted from its sublimation.[7)] Judging from these results, it is obvious that the pyrolysis of tetrasulfur tetranitride is accelerated in the presence of sulfur.

The tetrasulfur dinitride and the sulfur were con-

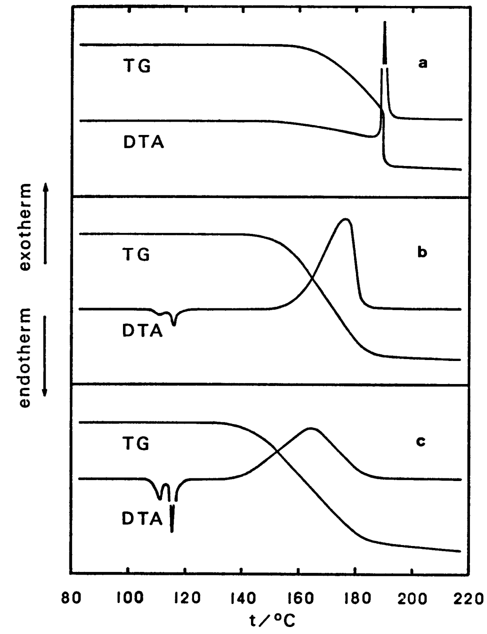

Fig. 2. DTA and TG patterns of pure and mixed S_4N_4.
a: pure, b: $n(S_4N_4)/n(S_8)=0.80$, c: $n(S_4N_4)/n(S_8)=0.20$

firmed as solid products during the pyrolysis of the mixed sample under an atmosphere of either argon or carbon dioxide by IR spectrophotometry[8] and by TLC.[9] Only nitrogen was identified as a gaseous product of the mixed sample by gas chromatography.

Stoichiometry of Products during Mild Pyrolysis of Tetrasulfur Tetraniride. The molar ratios of the pyrolysis products, $n(S_4N_2)/n(S_4N_4)$ and $n(N_2)/n(S_4N_4)$, were determined in order to elucidate the degradation process of tetrasulfur tetranitride mixed with sulfur. The symbols $n(S_4N_2)$ and $n(N_2)$ designate the moles of tetrasulfur dinitride and nitrogen produced, and $n(S_4N_4)$, the moles of pyrolyzed tetrasulfur tetranitride. The amount of the sample used in the experiment did not affect these molar ratios under the specified conditions; for instance, samples ranging from 102 to 221 mg(molar ratio of $S_4N_4=0.20$), when pyrolyzed at 130 °C for 60 min, gave essentially constant values of $n(S_4N_2)/n(S_4N_4)=0.58\pm0.01$ and $n(N_2)/n(S_4N_4)=1.36\pm0.01$. The values of $n(N_2)/n(S_4N_4)$ were slightly smaller than those calculated from the mass balance because some nitrogen bubbles remained in the molten sample. Reaction times between 40 and 120 min at 125 °C also had little effect on the above molar ratios.

Figure 3 shows that the $n(S_4N_2)/n(S_4N_4)$ ratio remained nearly constant for a given temperature of pyrolysis regardless of the variation in the original composition of the sample, whereas the amount of tetrasulfur dinitride produced increased at high contents of sulfur. The value of $n(S_4N_2)/n(S_4N_4)$ approached unity with a lowering of the temperature of pyrolysis. A decrease in this ratio at higher temperatures arose from the thermal instability of tetrasulfur dinitride.[4] A predominant decomposition of tetrasulfur tetranitride to its elements in the presence of sulfur should yield a value of $n(S_4N_2)/n(S_4N_4)$ much smaller than unity, even at low temperatures of pyrolysis. Based on these observations, the dominant pyrolytic process of tetrasulfur tetranitride mixed with sulfur can be expressed as:[10]

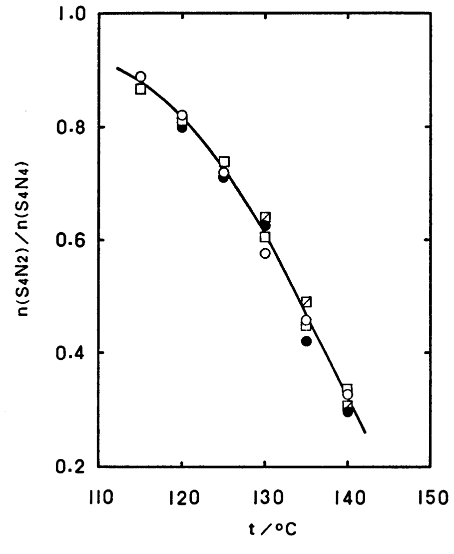

Fig. 3. Molar ratios of produced S_4N_2 at different temperatures.
Molar ratios of original samples, $n(S_4N_4)/n(S_8)$, are 0.65 (▨), 0.50 (●), 0.35 (□), and 0.20 (○), respectively.

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

$$S_4N_2 = \frac{1}{2}S_8 + N_2. \qquad (2)$$

Enthalpy Change during Pyrolysis of Tetrasulfur Tetranitride. The final products of either pure tetrasulfur tetranitride or of samples containing sulfur were identfied as sulfur and nitrogen when the pyrolysis was carried out in a closed system. Therefore, assuming the temperature dependence of the heat of decomposition to be negligible, the heat of decomposition (q) during the complete pyrolysis yields the standard enthalpy of the formation of tetrasulfur tetranitride, $\Delta H_f^\circ(S_4N_4)$, according to:

$$\Delta H_f^\circ(S_4N_4) = \frac{q}{a} + 2RT + \frac{1}{2}\Delta H_{\mathrm{trans}}(S_\mu) + \frac{1}{2}\Delta H_{\mathrm{fus}}(S_\lambda), \qquad (3)$$

where a are the moles of the tetrasulfur tetranitride, and $\Delta H_{\mathrm{trans}}(S_\mu)$ and ΔH_{fus} (S_λ) are the enthalpies of the transition from S_λ to S_μ [13.3 kJ mol^{-1} (as S_8 unit)][11] and of the fusion of S_α [17.0 kJ mol^{-1} (as S_8 unit)][11] respectively. Table 1 shows the results obtained according to Eq. 3 for the decomposition of tetrasulfur tetranitride in a closed system over the temperature range from 115 to 220 °C. The $\Delta H_f^\circ(S_4N_4)$ was estimated to be 469 ± 1 kJ mol^{-1}, which agreed well with the value reported by Barker *et al.*,[12] 460 ±8 kJ mol^{-1}.

When the pyrolysis of the mixed sample is interrupted, Eqs. 1 and 2 show that a moles of tetrasulfur tetranitride will change to $(a-x)$ moles of tetrasulfur dinitride,$(a+x)$ moles of nitrogen, and $x/2$ mol of sulfur (as S_8 units). Assuming that the tetrasulfur dinitride

Table 1. Standard enthalpy of formation of tetrasulfur tetranitride

Molar ratio of S_4N_4	$a=n(S_4N_4)\times 10^7$ / mol	$q\times 10^3$ / J	$\Delta H_f^\circ(S_4N_4)$ / kJ mol^{-1}
1.00	12.1	546	472
1.00	7.87	355	471
0.80	8.52	381	467
0.80	8.52	381	467
0.80	9.33	420	470
0.65	8.95	403	470
0.65	10.4	472	474
0.65	11.3	502	464
		Average	469±1

Table 2. Enthalpy of formation of gaseous tetrasulfur dinitride

Molar ratio of S_4N_4	$a=n(S_4N_4)\times 10^7$ / mol	$(a-x)=n(S_4N_2)\times 10^7$ / mol	$q\times 10^3$ / J	$\Delta H_f(S_4N_2)$ / kJ mol^{-1}
0.80	6.64	1.50	249	349
0.80	4.78	1.17	175	360
0.80	8.40	1.65	322	354
0.65	5.44	1.31	201	353
0.65	6.67	1.15	262	343
0.65	14.7	3.80	537	344
			Average	351±3

thus produced is in the gaseous state under the present experimental conditions, the enthalpy of the formation of gaseous tetrasulfur dinitride, $\Delta H_f(S_4N_2)$, is given by:

$$\Delta H_f(S_4N_2) = \left[a\Delta H_f^\circ(S_4N_4) - q - (a+x)RT - \frac{x}{2}\Delta H_{\mathrm{trans}}(S_\mu) - \frac{x}{2}\Delta H_{\mathrm{fus}}(S_\lambda)\right]\Big/(a-x), \tag{4}$$

where q is the heat of decomposition observed on the interrupted pyrolysis during the DSC measurement. On reaching ≈175 °C, which is the approximate peak temperature of the exothermic change, the sample container was immediately removed from the DSC equipment to stop the pyrolysis, and then the solid quickly dissolved in a small volume of carbon tetrachloride, followed by the spectrophotometric determination of species.

Table 2 shows the results obtained according to Eq. 4. The $\Delta H_f(S_4N_2)$ was estimated to be 351±3 kJ mol^{-1}, which was nearly constant regardless of the difference in the composition of the samples.

Discussion

Tetrasulfur dinitride can be prepared by several processes,[13—15] including the pyrolysis of tetrasulfur tetraimide.[9] Tetrasulfur tetranitride degrades easily to tetrasulfur dinitride in the presence of sulfur, whereas the vapor at a low pressure in the absence of sulfur dissociates to disulfur dinitride, S_2N_2, around 250 °C.[16,17] For example, the degree of decomposition of a sample kept at 130 °C for 60 min increased from 18 to 53% when the molar ratio of sulfur was raised from 0.20 to 0.80, while the $n(S_4N_2)/n(S_4N_4)$ ratio remained constant(0.59—0.61). A step-by-step degradation was confirmed by the quantitative relationship of the pyrolysis products of the mixed sample as a function of the temperature.

Table 3. Bond lengths and bond energies in tetrasulfur dinitride

Bond	Bond length[21] r/pm	Bond energy, E/kJ mol^{-1} Calcd(1)[a]	Bond energy, E/kJ mol^{-1} Deducd(2)
S–S	206.1	262	257[22]
S–N	167.1	250	247[b]
S=N	156.1	339	352[b]
$\Delta H_f[S_4N_2(1)]$/kJ mol^{-1}		361	
$\Delta H_f[S_4N_2(2)]$/kJ mol^{-1}		350	
$\Delta H_f[S_4N_2$(This work)]/kJ mol^{-1}		351±3	

a) Calculated according to Sanderson's method.[20] b) Deduced from the linear correlation between the bond lengths and bond energies of the S≈N bonds.

Using the standard enthalpy of the formation of tetrasulfur tetranitride, $\Delta H_f^\circ(S_4N_4)$, of 469±1 kJ mol^{-1}, the standard enthalpies of the formation of atomic nitrogen and sulfur (473 and 279 kJ mol^{-1} respectively),[18] and the enthalpy of sublimation (89 kJ mol^{-1}),[7] the S–N bond energy (nominal bond order, $n=1.5$) in tetrasulfur tetranitride was calculated to be 306 kJ mol^{-1}, which is close to the values reported by Barker *et al.* (308 kJ mol^{-1})[12] and by Fleig and Becke-Goehring (301 kJ mol^{-1}).[19]

The calculations described by Sanderson[20] gave the S–S, S–N, and S=N bond energies in the six-membered ring molecule of tetrasulfur dinitride as 262, 250, and 339 kJ mol^{-1} respectively, as is shown in Table 3. Based on these bond energies and the standard enthalpies of the formation of atomic nitrogen and sulfur,[18] the enthalpy of the formation of gaseous tetrasulfur dinitride, $\Delta H_f[S_4N_2\ (1)]$, was calculated to be 361 kJ mol^{-1}.

The bond energies can also be deduced from other known parameters. The S–S bond length and the S–S–S bond angle (206.1 pm and 102.9°)[21] in tetrasulfur dinitride are very close to those in cyclohexasulfur, S_6, (205.7 pm and 102.2°),[22] so that the S–S bond energy in tetrasulfur dinitride can assumed to be the same as in cyclohexasulfur (257 kJ mol^{-1}).[23] From the linear relationships between the bond lengths and the bond energies of the S≈N bond [158 pm[24] and 335 kJ mol^{-1} [19] for $S_3N_2O_2$ ($n=2$), 161.6 pm[25,26] and 306 kJ mol^{-1} for S_4N_4 ($n=1.5$), and 167.4 pm[27,28] and 249 kJ mol^{-1} [19] for $S_4(NH)_4$ ($n=1$)], the S–N and S=N bond energies in tetrasulfur dinitride were deduced to be 247 and 352 kJ mol^{-1} respectively, as is shown in Table 3. These latter values, combined with the deduced S–S bond energy and the standard enthalpies of the formation of atomic nitrogen and sulfur,[18] gave the enthalpy of the formation of gaseous tetrasulfur dinitride, $\Delta H_f[S_4N_2\ (2)]$, of 350 kJ mol^{-1}. The corresponding value obtained in this work (351±3 kJ mol^{-1}) agrees exceedingly well with those calculated above and by Sanderson.[20]

Tetrasulfur dinitride has a melting point of 23.5 °C,[29] and it gives a viscous liquid on melting. The vapor pressure of the latter and the enthalpy of vaporization have not been reported. Heal[1] mentioned that tetrasulfur dinitride evaporated easily at 30—40 °C under a pressure of 670 Pa. Sato[30] showed that the enthalpy of vaporization for a normal liquid, ΔH_{vap}, could be calculated (to within an error of 5%) from the following equation, which was derived from Hildebrand's rule:

$$\frac{\Delta H_{\mathrm{vap}}}{T} = 176.8\left(\frac{p}{T}\right)^{-0.119}, \qquad (5)$$

where p is the vapor pressure and T, the absolute temperature. Assuming that Eq. 5 is applicable to liquid tetrasulfur dinitride and that its vapor pressure is 670 Pa at 35 °C, the enthalpy of vaporization was calculated to be 50 kJ mol^{-1}. Consequently, the standard enthalpy of the formation of tetrasulfur dinitride, $\Delta H_f^\circ(S_4N_2)$, was estimated to be 301 kJ mol^{-1}, involving an uncertainty caused by the lack of a reliable value of the enthalpy of vaporization.

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