The Differential Scanning Calorimetry of 1,3,5,7,2,4,6,8-Tetrathiatetrazocine

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Synopsis. The molar heat of the decomposition of $S_4(NH)_4$ was obtained as 360±7 kJ mol^{-1} by means of differential scanning calorimetry. This value gave the standard enthalpy of the formation, $\Delta H_f(S_4(NH)_4, s, 298.15\,K)$, as 318±7 kJ mol^{-1}, which was comparable with that calculated (311 kJ mol^{-1}).

1,3,5,7,2,4,6,8-Tetrathiatetrazocine (tetrasulfur tetraimide, $S_4(NH)_4$) is finally pyrolyzed into sulfur, ammonia, and nitrogen in an argon atmosphere through step-by-step degradation.[1] However, little information on the thermodynamic properties is available, in contrast to those of tetrasulfur tetranitride (S_4N_4)[2,3] and tetrasulfur dinitride (S_4N_2).[2] In this work, the pyrolysis of this compound was studied by means of differential scanning calorimetry (DSC).

Experimental

The $S_4(NH)_4$ was prepared and purified by the method described in a previous paper.[1]

The heat of the decomposition of $S_4(NH)_4$ was measured at the heating rates of 16 and 32 K min^{-1} with a Perkin-Elmer, model DSC-1B, differential scanning calorimeter. The sample was carefully weighed with a microbalance and then tightly sealed in an aluminium container in an argon atmosphere. The DSC equipment was calibrated with an indium of 99.999% purity.

The molar heat capacity, C_p, of this compound was measured at the fixed heating rate of 8 K min^{-1} with the same equipment, using quartz as a reference. The sufficient reliability of this method was indicated by the agreement between the observed and the reported molar heat capacities of α-sulfur[4] (±1.4%) over the tempetarure range from 328 to 368 K.

Results and Discussion

Measurement of Heat of Decomposition of $S_4(NH)_4$. Figure 1 shows the DSC curve of $S_4(NH)_4$ taken at the heating rate of 16 K min^{-1} in the argon atmosphere. The DSC pattern consisted of sharp and broad exothermic peaks, in addition to an endothermic peak caused by its fusion. The former two peaks were attributable to the step-by-step degradation.[1] The dotted line in Fig. 1 was taken as the base line for estimating the heat of decomposition. The degradation immediately occurred after its fusion at the heating rates applied, though it took place even before fusion at such slow heating rates as 3 K min^{-1}.[1] Thus, the overall heat of decomposition was defined as the corresponding area by subtracting the endothermic peak area from the exothermic one in Fig. 1.

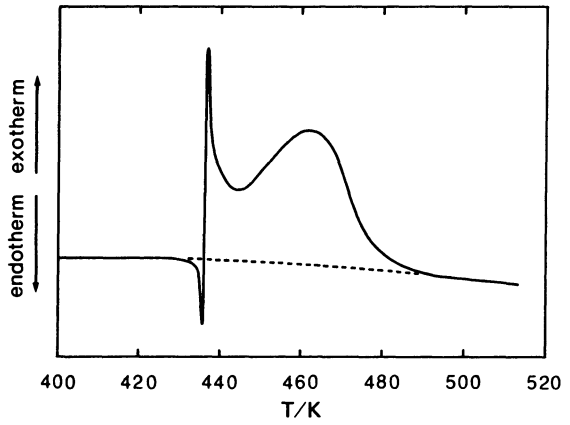

Fig. 1. DSC pattern of $S_4(NH)_4$ at heating rate of 16 K min^{-1}.

The molar heat of decomposition, Q, was obtained as 360±7 kJ mol^{-1} as the average for nine runs; the uncertainty value was defined as $\pm 3.0\sigma/\sqrt{n}$, where σ and n are the standard deviation and the number of data respectively. The value of Q was scarcely changed at either heating rate, i.e., 16 or 32 K min^{-1}, within the limits of experimental error shown above.

The molar heat capacity, C_p, of $S_4(NH)_4$ was measured over the temperatures from 328 to 363 K at the heating rate of 8 K min^{-1}. No chemical change in the sample was confirmed by thin-layer chromatography for 20 min after each run. Measurements below 323 K did not give reproducible results because of unstable base lines. The linear temperature dependence ($C_p = 0.153 + 1.26\times10^{-4}T$) gave the value of C_p as 0.191 kJ mol^{-1} K^{-1} at 298.15 K.

On the basis of stoichiometric correlation,[1] the overall pyrolytic reaction can be expressed as:[5]

$$S_4(NH)_4 = 1/2S_8 + 4/3N_2 + 4/3NH_3 \quad (1)$$

According to Eq. 1, the following equation yields the standard enthalpy of the formation of $S_4(NH)_4$:

$$\Delta H_f(S_4(NH)_4, s, 298.15\,K) = Q + 8/3RT + 1/2(\Delta H_t(\alpha, \beta) + \Delta H_m(\beta, \lambda) + X\Delta H_p) + 4/3\Delta H_f(NH_3, g, 298.15\,K) - \int_{298.15}^{T} \Delta C_p dT \quad (2)$$

where $\Delta H_t(\alpha,\beta)$ and $\Delta H_m(\beta,\lambda)$ are the enthalpy changes of transition from S_α to S_β (3.2 kJ mol^{-1})[6,7] and of the fusion of S_β (13.8 kJ mol^{-1});[6,7] ΔH_p, the enthalpy change of polymerization from S_λ to S_μ (13.3 kJ mol^{-1});[6,7] X, the fraction of S_μ (0.228 at 464 K);[8] $\Delta H_f(NH_3, g, 298.15\,K)$, the standard enthalpy of the formation of ammonia (−45.9 kJ mol^{-1}),[6] and ΔC_p, the difference in the molar heat capacities between the initial and final states.[6] The reaction temperature, T, was taken as 464 K at the maximum of the broad exothermic peak (Fig. 1), and the integral term was calculated as −1.5 kJ mol^{-1}.

According to Eq. 2, the standard enthalpy of the

formation of $S_4(NH)_4$, $\Delta H_f(S_4(NH)_4, s, 298.15\,K)$, was obtained as 318 ± 7 kJ mol^{-1}.

Calculation of Standard Enthalpy of the Formation of $S_4(NH)_4$. Sanderson's method[9] gave the S–N and N–H bond energies in $S_4(NH)_4$ as 247.7 and 363.8 kJ mol^{-1}, based on their respective bond lengths of 167.4[10] and 108 pm.[11] By combining these values with the standard enthalpies of the formation of atomic sulfur, nitrogen, and hydrogen,[12] the enthalpy of the formation of gaseous $S_4(NH)_4$, $\Delta H_f(S_4(NH)_4, g, 298.15\,K)$, was calculated as 426 kJ mol^{-1}.

The enthalpy of sublimation, ΔH_{sub}, is given as:[13]

$$\Delta H_{sub} = L^0 + RT \quad (3)$$

where L^0 is the lattice energy at 0 K. The lattice energy of the $S_4(NH)_4$ crystal was estimated by means of the Slater-Kirkwood equation,[14] assuming that the lattice energy is nearly equal to the London dispersion force, E, ($L^0=-E$),[13] and that the effect of hydrogen bonds in the crystal is negligible.[11] To calculate the value of E, the polarizabilities, α, of sulfur, nitrogen, and hydrogen atoms were taken as 2.836×10^{-24}, 9.437×10^{-25}, and 4.152×10^{-25} cm^3 respectively, which were deduced by the use of the Clausius-Mossotti relationship using corresponding atomic refractions.[15] Taking the 306 pairs of interatomic distances (less than 500 pm) which were given by the atomic coordinates,[10,11] the value of the ΔH_{sub} of $S_4(NH)_4$ was estimated as 115.0 kJ mol^{-1} ($E=-112.5$ kJ mol^{-1}).

For checking the reliability of this calculation, the enthalpies of the sublimation of tetrasulfur tetranitride and α-sulfur were also estimated in the same way.[16–18] The values thus calculated were 88.0 and 106.4 kJ mol^{-1} respectively; these values agreed closely with those observed (88.7[19] and 105.9 kJ mol^{-1} [12]).

The standard enthalpy of the formation, $\Delta H_f(S_4(NH)_4, s, 298.15\,K)$, was given as 311 kJ mol^{-1}, combined with the enthalpies of the formation at the gaseous state and of the sublimation. Consequently, the calculated value was in fair agreement with that obtained in this work (318 ± 7 kJ mol^{-1}).

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