Mechanism for thermal decomposition of 1H-tetrazole

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Thermal decomposition of 1H-tetrazole has been carried out at various heating rates and various end point temperatures. A pyroprobe was used as a heating device and the decomposition products have been analyzed by FT-IR.

As a result, the two different mechanisms for the thermal decomposition of 1H-tetrazole are proposed depending on the decomposition temperature. At the lower decomposition temperature, 1H-tetrazole can be thought to induce only the cleavage of C5-N1 and N3-N4 bonds, because HCN and HN_3 are detected as decomposition products. On the other hand, at the higher decomposition temperature, various decomposition reactions may occur simultaneously to form such products as HCN, NH_3, CH_4 and C_2H_2.

1. Introduction

Recently tetrazoles received much paid attention as new energetic materials. Figure 1 shows their general structure. Some studies on the thermal decomposition of tetrazoles have been reported since 1950[1-3].

The thermal decomposition of 1H-tetrazole was studied at heating rates of 0.6~20 K/min using differential scanning calorimetry (DSC) by Lesnikovich et al[2]. He reported the melting point of 155~161 ℃, the decomposition temperature of 170~174 ℃ and the activation energy for the decomposition of 152~178 kJ/mol. By analysis
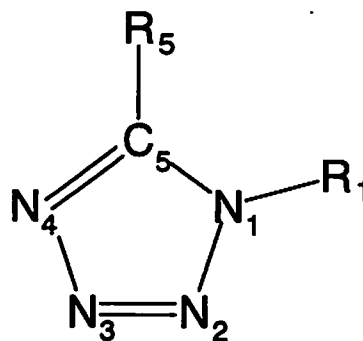

Fig. 1 Structure of tetrazoles

of the decomposition products, it was clarified that 1H-tetrazole decomposes to give HCN and HN_3 under some conditions and to give a polymer under other conditions.

The flash thermolysis of 1H-tetrazole was studied by Guimon et al.[4] and the products were analyzed using HeI (He resonance line is used as light source) photoelectric spectroscopy. In his paper, he tried to clarify the decomposition mechanism based on molecular orbital calculations.

The thermal decompositions of six kinds of tetrazoles were studied by Wu et al.[5] using the Curie point pyrolyzer at the lower temperature range around 300 ℃ and in the higher temperature range around 750 ℃. The mechanism for the thermal decomposition in these two different

1H-tetrazole (R=H)

$$\longrightarrow CH_3CN + HN_3$$

5-Methyl-tetrazole (R=CH₃)

$$\longrightarrow HCN + HN_3$$

Fig. 2 The decomposition products of tetrazoles at lower temperature

Fig. 3 Brill cell and Pyroprobe 2000

temperature ranges was suggested. At the higher temperatures, intermediates found during pyropysis further decomposed to give reactive chemical species that generated many kinds of products. In the lower temperature range, N_2, HCN and HN_3 were detected from the 1H-tetrazole, and CH_3CN and HN_3 were detected from 5-methyl-tetrazole as the decomposition products. The decomposition products of tetrazoles at lower temperature are shown in Figure 2.

The energy given to the tetrazoles under storage conditions may be different depending on the handling conditions. The decomposition mechanism should then be different depending on the handling conditions. However, a systematic study on the decomposition mechanism for tetrazoles has not been carried out from the standpoint of the given energy.

Therefore, in order to obtain some knowledge on the thermal decomposition mechanism under different given energies, we have attempted to study the thermal decomposition of 1H-tetrazole at different heating rates and end point temperatures using a pyroprobe as a heating device. This paper describes the decomposition mechanism obtained from the experiment for different heat inputs.

2. Experiment

1H-tetrazole (abbreviated as 1HT hereafter) possessing a hydrogen atom both at the 1- and 5-positions was used as a typical tetrazole for the thermal decomposition. About 2 mg of 1HT was decomposed in a Brill cell under an atmosphere of nitrogen using a pyroprobe (Pyroprobe 2000, CDS
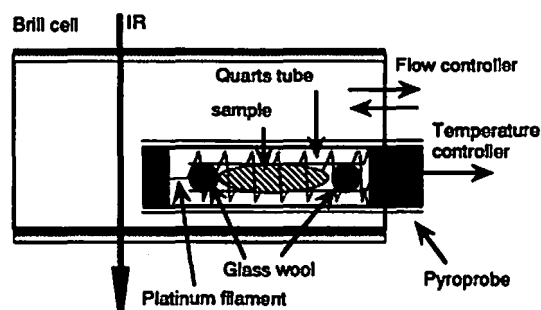
Analytical Inc.). The setup for the Brill cell in the pyroprobe is shown in Figure 3. The decomposition products were identified and their concentrations were determined by FT-IR (MAGNA-IR 850, Nicolet Instrument Corporation).

As the heating rates of the pyroprobe, (a) 1,000 K/s, (b) 100 K/s, (c) 10 K/s, and (d) 1 K/s were used. The influence of the end point temperature on the decomposition products has also been examined at the heating rate of 10,000 K/s. The end point temperature was changed from 300 ℃ to 1,000 ℃. Furthermore, the measurements were carried out at 15 K/s and 12 K/s in order to confirm the results and assumptions. The FT-IR was operated with a resolution of 2 cm^{-1}, a sampling interval of 0.6 seconds and four integration times. The heating programs are shown in Figures 4. The operating conditions were determined by taking into consideration that the melting point was 150 ℃ and the initial DSC (T_{DSC}) was 201 ℃ decomposition temperature.

The time – concentration profiles of the products were observed from the start of the decomposition.

3. Results and Discussion

3. 1 Effects of heating rate

Figure 5 shows the profiles of the decomposition products at the heating rate of 1,000 K/s, 100 K/s, 10 K/s and 1 K/s. The profiles are represented by IR relative absorbance of products vs. time after reached decomposition temperature. IR relative absorbance means integration quantity of product and it corresponds to concentration. Since calibration curves could not be prepared as to HN_3 and C_2H_2, their absorbance values were used to describe the distribution of the decomposition products
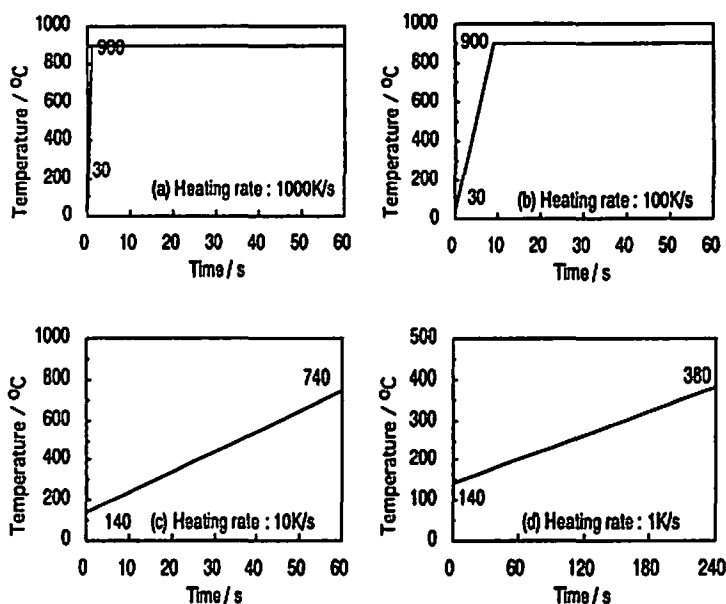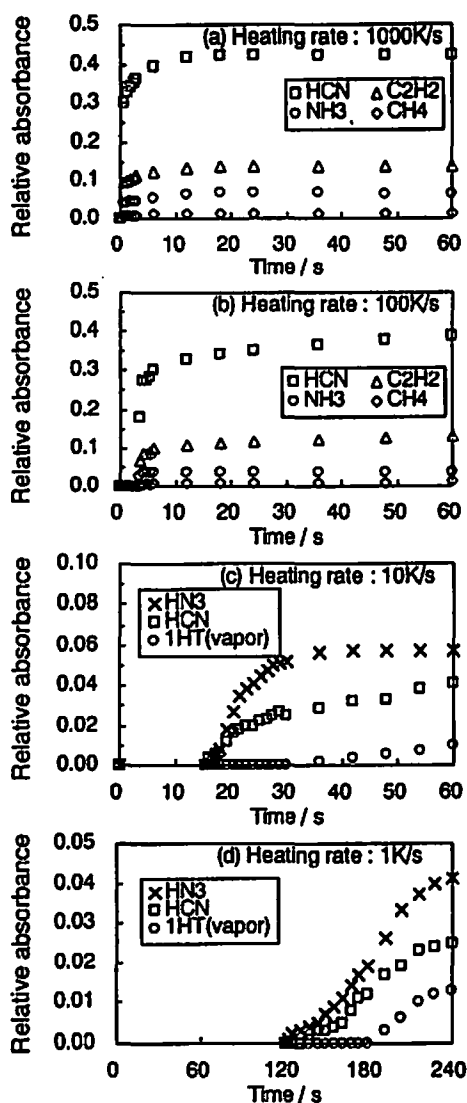
Fig. 4 Program of heating

Fig. 5 IR relative absorbance of products v.s. time
after reached at decomposition temperature

instead of their concentrations. N_2 could not be detected because of their IR inactiveness.

For (a) and (b), HCN, NH_3, CH_4 and C_2H_2 were detected as the initial decomposition products at the higher heating rates. It may be difficult to determine the exact time and temperature for the initial decomposition because of the delay time caused by the heat conduction in the sample, gas diffusion and sampling intervals. As for HCN, however, the gas evolution rate is higher and the volume of gas is larger at the higher heating rates than that at the lower heating rates (Figure 5).

For (c) and (d), HCN and HN_3 were detected as the initial decomposition products at the lower heating rates. The decomposition temperatures at which the initial decomposition products are detected can be estimated from the heating program. They were 297 ℃ for (c) and 262 ℃ for (d). Since the absorbance at 10 K/s rises quickly, It can be said that the gas evolution at the heating rate at 10 K/s was faster than that at 1 K/s.

These results suggest that the thermal decomposition mechanism for 1HT should change at the heating rate between 10 K/s and 100 K/s. Therefore, the thermal decomposition of 1HT was carried out at the heating rate of 15 K/s in order to obtain some information on the temperature at which the mechanism might change. The time - absorbance profiles of the decomposition products at the
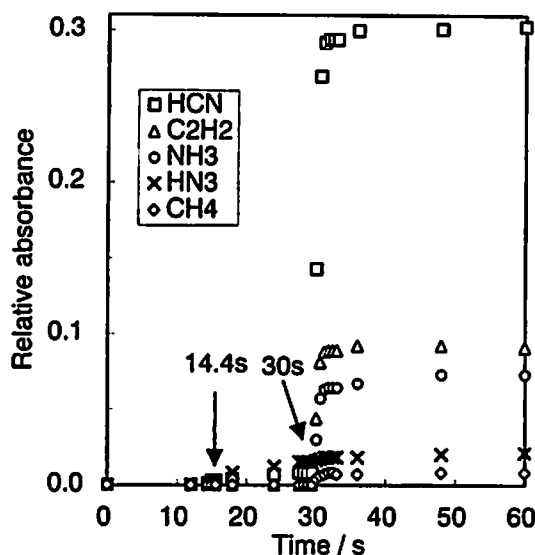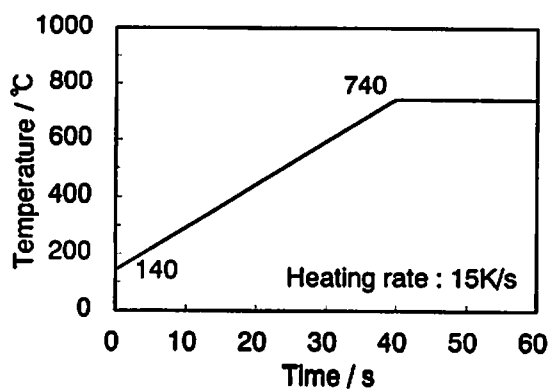
Fig. 6 Program of heating at 15 K/s and IR relative absorbance of products vs. time after reached decomposition temperature

Fig. 7 The product distributions at each decomposition temperature

heating rate of 15 K/s are shown in Figure 6. Low concentrations of HCN and HN_3 were detected after 14.4 second (corresponding to 356 ℃) from the beginning of the heating and then their concentrations gradually increased. CH_4, C_2H_2, NH_3 and a high concentration of HCN were detected after 30.0 second (corresponding to 590 ℃).

These results indicate that at the lower heating rates, 1HT gradually decomposes at 260~360 ℃ to give HCN and HN_3 and that at the higher heating rates, it rapidly decomposes to give HCN, NH_3, CH_4 and C_2H_2. When the measurement was carried out at 12 K/s, the same change took place.

3. 2 Influence of end point temperature

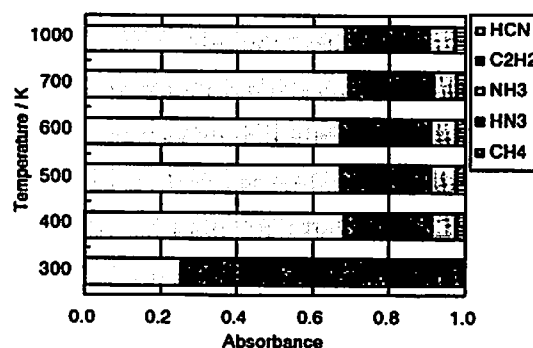The product distributions at each decomposition temperature are shown in Figure 7. In order to understand the absorbance tendencies, sum of the absorbance was normalized to 1. The decomposition products at greater than 400 ℃ were different from those at 300 ℃. At 300 ℃, HCN and HN_3 were detected as the major products. At temperatures higher than 400 ℃, NH_3, CH_4, and C_2H_2 were detected instead of HN_3. Therefore, the decomposition mechanism may differ depending on the end point temperature. The decomposition temperature at each reaction was estimated from the heating rate and the time when the products were detected.

Taking into account the influence of the heating rate and end point temperature, two stages of decomposition exist for 1HT. In one of the stages, 1HT gradually decomposes to give HCN and HN_3. It occurs at the lower temperature so that it was observed at the lower heating rates. The other stage occurs at the higher temperature, where HCN, NH_3, CH_4 and C_2H_2 are rapidly generated. The process was observed at the higher heating rates. These results are summarized in Table 1.

In the lower temperature stage, 1HT initiates the decomposition by cleavage of N1-C5 and N3-N4 bonds at certain temperatures. There may be some delay time in the observation due to the heat conductivity and gas diffusion velocity. If the delay time was neglected, as the heating rate increased, the low temperature stage starts at higher temperature.

On the other hand, the decomposition temperature during the high temperature stage became lower as the heating rate increased. It was postulated that at the high temperature stage, the cleavage of its comparatively strong bonds may be involved in the decomposition. The heat of formation for HCN, HN_3 and 1HT are 130.5 kJ/mol, 294.1 kJ/mol and 237.2 kJ/mol, respec-

Table 1 Decomposition temperature at each heating rate

Heating rate [K/s]	low temperature stage Decomposition temperature of HCN and HN₃ production	high temperature stage Decomposition temperature of HCN, NH₃, CH₄ and C₂H₂ production
1	261~262 ℃	
10	291~297 ℃	
12	296~303 ℃	632~639 ℃
15	347~356 ℃	581~590 ℃
10000		below 400 ℃

tively. Therefore, the reaction during the low temperature stage should be endothermic. On the other hand, the heat of formation for C_2H_2, CH_4 and NH_3 are 226.8 kJ/mol, -74.9 kJ/mol and -45.6 kJ/mol, respectively, so the reaction during the high stage reaction should be exothermic. Although the decomposition during the high temperature stage is endothermic, the high temperature stage may be induced when the reactants obtain sufficient energy to surpass the endothermic reaction velocity during the low temperature stage. Therefore, the decomposition temperature became lower during the high temperature stage as the heating rate increased.
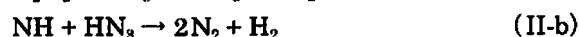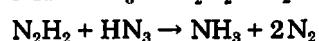
3. 3 Thermal decomposition mechanism

During the low temperature reaction, 1HT decompose to form HCN and HN_3. These products can be easily produced from the cleavage of N1-C5 and N3-N4 cleavage (Figure 2). During the high temperature reaction, 1HT decomposed to form CH_4, C_2H_2, NH_3, and HCN. Part of the reactions during the high temperature stage appeared to be same as in the low temperature reaction because HCN was detected from both of them. However, NH_3 was detected instead of HN_3 that is simultaneously generated with HCN in the low temperature stage. The difference in products depends upon their reaction temperature. As the decomposition temperature increases, HN_3 may decompose to give H_2, N_2, and NH_3. The following initial decomposition step was proposed by Meyer et al.[6]

$$HN_3 \rightarrow NH + N_2 \qquad (I)$$

NH reacts with HN_3 and produces NH_3 or N_2. From Meyer's results, 94% of NH generates NH_3

(step II-a), and 6% of NH makes H_2 (step II-b).

$$NH + HN_3 \rightarrow N_2H_2 + N_2 \qquad (II\text{-}a)$$
$$N_2H_2 + HN_3 \rightarrow NH_3 + 2N_2$$
$$NH + HN_3 \rightarrow 2N_2 + H_2 \qquad (II\text{-}b)$$

HN_3 (singlet: ground state) and the HN_3 biradical (triplet: excited state) were inferred to behave as reactants in step I. They appeared to be directly produced from 1HT. Based on the proposed mechanism, the structures of 1HT, the decomposition products and their transition states were optimized and their enthalpies were calculated with the GAUSSIAN 94/PM3 method. Figure 8 shows the enthalpy level diagram of the species based on a tetrazole. The scheme indicates that the reaction is endothermic and the activation energy for the HN_3 generating path is estimated as 226 kJ/mol. This
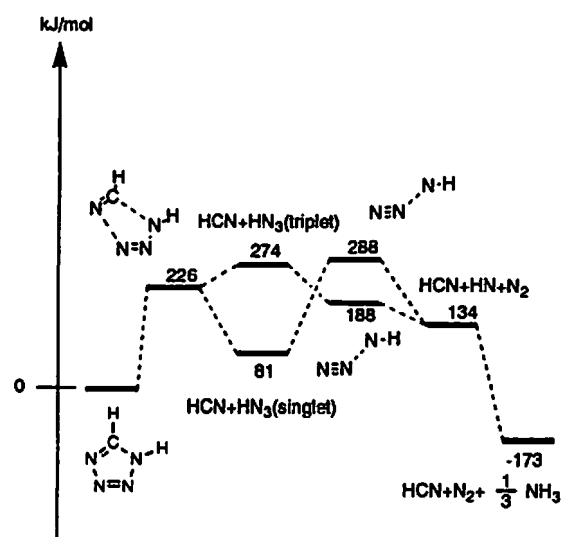

Fig. 8 Enthalpy diagrams of decomposition species calculated by GAUSSIAN 94/PM3 method. (based on a tetrazole)
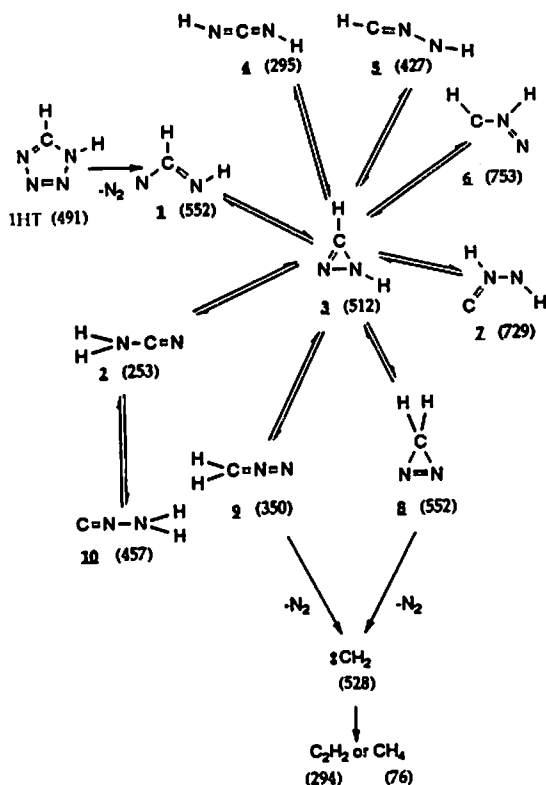
Fig. 9 The decomposition scheme of tetrazoles
The values in parentheses are enthalpies (kJ/mol).

Fig. 10 Enthalpy diagrams of decomposition species for high temperature reaction (based on a tetrazole)

decomposition does not occur without heating.

Furthermore, 207 kJ/mol is required if HN_3 (singlet) proceeds to step I. On the other hand, HN generation from the HN_3 biradical (triplet) occurred easier because the energy of the HN_3 biradical (triplet) was higher than that of HN_3 (singlet). In other words, molecular orbital calculation suggested that the reaction via HN_3 biradical (triplet) occurred easier than via HN_3 (singlet). One hypothesis that explains why NH_3 was detected only at the higher decomposition temperature is that the HN_3 biradical (triplet) could be formed and activates the NH_3 directly under these conditions.

Although CH_4 and C_2H_2 were detected during the high temperature stage, they did not appear in the proposed mechanism. Since CH_4 and C_2H_2 cannot be directly formed from 1HT, it can be thought that radicals may be formed by bond cleavage and recombine to give CH_4 and C_2H_2. To clarify the radical formation, some decomposition pathways were proposed. Figure 9 shows the relationship of 1HT and the imaginary and real decomposition products, which are the revised and recalculated one
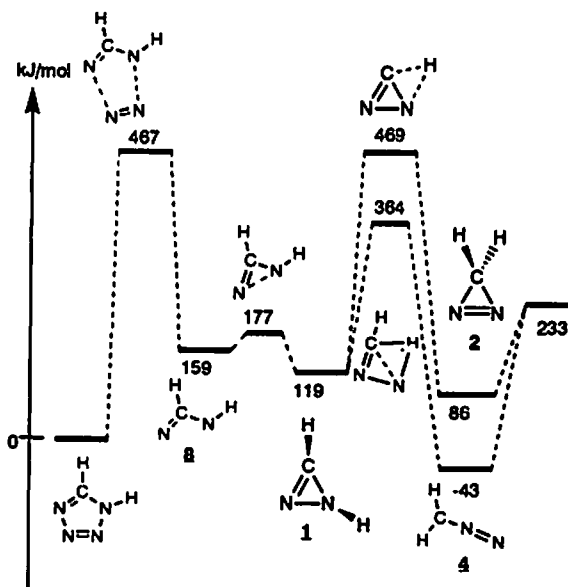
of Guimon et al.[1] All the species are revealed as ground state one by frequency analysis.

In view of the chemical structure, it is assumed that CH_4 and C_2H_2 should be generated via isomer 8 or 9. The calculated enthalpies support the rational of the existence of two isomers. Figure 10 shows the enthalpy diagrams of decomposition species for the most reasonable reactions in the high temperature stage. Higher energy is need for the N1-N2 bond fission than the N1-C5 bond fission.

4. Conclusion

A mechanism for the thermal decomposition for 1HT has been suggested under two different heating conditions. At the lower heating rates, 1HT may decompose only by the cleavage of the C5-N1 and N3-N4 bonds, because HCN and HN_3 were detected as decomposition products. At the higher heating rates, many reactions may simultaneously occur to form products such as HCN, NH_3, CH_4 and C_2H_2. Investigation of the influence of the decomposition temperature indicated that decomposition temperature changed decomposition mechanism. The semi-empirical calculation clarified that the difference depended upon the energy level of the reactants, products, and intermediates. Whereas during low temperature stage, 1HT directly releases HN_3, HN_3 is activated and reacts further during

the high temperature stage. CH_4 and C_2H_2 were characteristic products in high temperature stage, and the calculated energies supported their formation from intermediates.

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1H-テトラゾールの熱分解機構に関する研究

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　種々の昇温速度や到達温度の条件下で, 1H-テトラゾールの熱分解実験を行った。実験に際してはパイロプローブを用いて試料を加熱し, FT-IRを用いて生成物分析を行った。その結果, 1H-テトラゾールの熱分解は, 分解温度によって2つの異なった機構が考えられた。低温においてはシアン化水素とアジ化水素が検出されたことから, テトラゾール環のC5-N1, N3-N4結合が解離していることが予想された。一方, 分解温度が高温の場合, シアン化水素, アンモニア, メタン, アセチレンが検出され, 複数の反応が同時に起こっていることが示唆された。

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