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EFFECTS OF SURROUNDING GAS PRESSURE ON THE DECOMPOSITION OF THIADIAZOLE COMPOUNDS

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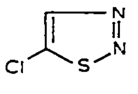
ABSTRACT

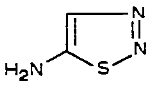
The decomposition characteristics of 5-chloro-1,2,3-thiadiazole (CT), 5-amino-1,2,3-thiadiazole (AT), and 5-acetylamino-1,2,3-thiadiazole (AAT) were investigated in atmospheres of nitrogen, helium, and air up to 5.0 MPa using pressure DSC and TG. CT evaporates in air or inert gas atmospheres at atmospheric pressure. However, by raising the surrounding gas pressure, CT began to exhibit an exothermic reaction even in inert gases and an explosive decomposition with a great evolution of heat occurred at relatively high pressures. AT and AAT exhibited exothermic decompositions in these gases at 1 atm. AT decomposed at low temperatures, but the evolution heats were not so much influenced by the pressure increase of nitrogen. AAT was the most heat-stable substance among the compounds studied and had almost a constant low decomposition heat inspite of the pressure. The activation energies of the decomposing chemicals were calculated from DSC and TG curves.

INTRODUCTION

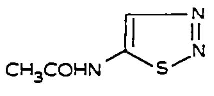
In 1980, vigorous explosions occurred in sequence at chemical plants in Japan used for the production of 5-chloro-1,2,3-thiadiazole (CT), or 5-amino-1,2,3-thiadiazole (AT). In one case it was a distillation process of CT and in the other a manufacturing process of AT from CT. AT, which is produced by the reaction of pressurized CT and ammonia, is said to be thermally unstable, but it is an important material for the manufacture of antibiotic substances. 5-Acetylamino-1,2,3-thiadiazole (AAT), which is derived from AT, is relatively thermally stable. Hence, from the point of view of safety of transportation or storage, in most cases AT may be converted to AAT, which is deacetylated prior to use for the manufacture of the required substances.



5-Chloro-1,2,3-thiadiazole



5-Amino-1,2,3-thiadiazole



5-Acetylamino-1,2,3-thiadiazole

CT has a melting point of about 20°C. It is worth noting that liquid CT has exploded or detonated under certain conditions, because liquid substances are apt to evaporate during heating under atmospheric pressure. A few studies have been reported on the evaluation of the thermal stability of reactive substances under pressures >1 atm in DTA, DSC, or TG. Nguyen et al. [1] examined the behavior of aqueous hydrogen peroxide in nitrogen by DSC at various pressures up to 6.6 MPa. Seyler [2] studied the pressure effects of some reactive chemicals using pressure DTA. Morisaki et al. [3] investigated the decomposition characteristics of sponge blowing agents for rubber or plastics by DSC and TG in air or inert gas atmospheres at various pressures up to 5.3 MPa. Generally, a surrounding gas pressure tends to increase the thermal hazard or reactive substances.

In this paper, the decomposition characteristics of CT, AT, and AAT at various pressure atmospheres were investigated with pressure DSC and TG by considering the thermal hazard evaluation.

EXPERIMENTAL

CT, AT, and AAT were supplied by Japan Hydrazine Co., and their purities were reported to be 97.8%, 93.7%, and 98.5%, respectively. A pressure differential scanning calorimeter (Du Pont Co.) was used to measure the decomposition heats of the thiadiazole compounds up to 5.0 MPa. A weighed sample (CT), ~2 mg, was placed in an aluminum cell (5 mm ϕ, 4 mm depth) with a cover, and a pin-hole was made on the sealed cover. AT or AAT (weighing about 0.6 mg) was packed into a non-hermetic aluminum pan (6.5 mm ϕ) with an aligned cover.

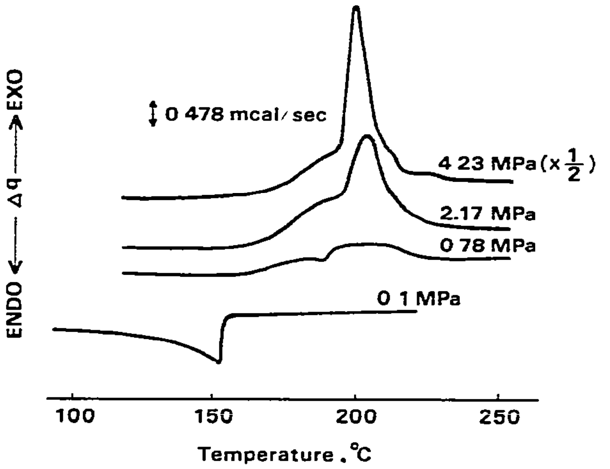
Pressure TG for the substances was carried out with a high pressure thermobalance (Rigaku Denki Co.) at pressures of 0.1—5.0 MPa; 5—10 mg of the sample were used for the TG experiments. The detailed procedures for the pressure TG have been reported in a previous paper [4]. CT was also sealed in an aluminum cell.

Before heating the samples, the DSC cell or the vessel of the thermobalance was flushed three times with the desired gas at 1.8 MPa and kept at constant pressure. The concentration of residual oxygen in the pressurized nitrogen in the DSC cell was confirmed to be less than 1 ppm by gas chromatography. Nitrogen, helium, or air was not passed over samples during linear heating at 2—50°C min^{-1} (DSC) or 1.25—20°C min^{-1} (TG).

RESULTS AND DISCUSSION

Decomposition heats of CT

Figure 1 shows DSC curves of CT in nitrogen at various pressures at 10°C min^{-1}. At atmospheric pressure, CT begins to evaporate at below 100°C and this endotherm is completed at 150°C with an evaporation heat of about 90 cal g^{-1}. An exotherm with a shoulder appears at 170—330°C at about 0.7 MPa. This exotherm becomes large as the surrounding gas pressure is increased. At 4.23 MPa, CT may undergo violent decomposition at around 190°C, leaving black carbonaceous products as a residue. Pressure DSC curves of CT in air are shown in Fig. 2. CT evaporates mostly in air at atmospheric



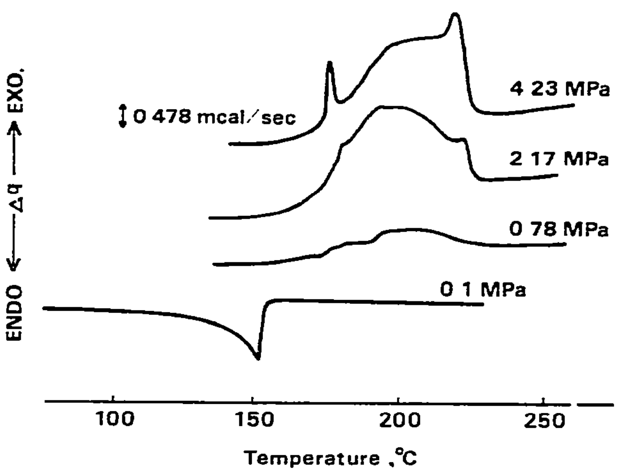


Fig. 1. DSC curves of CT in nitrogen at various pressures. Heating rate: 10°C min^{-1}.

Fig. 2. DSC curves of CT in air at various pressures. Heating rate· 10°C min^{-1}.

pressure when heated to 10°C min^{-1}. The exotherms have a tendency to become large with increase of air pressure, but the presence of oxygen may complicate the reaction mechanism. The pressure DSC curves are characterized by two exothermic peaks at about 180°C and 220°C under the high air pressures.

The decomposition heats of CT in nitrogen or air, which were calibrated from the heat of fusion of In, are plotted against the pressure for the

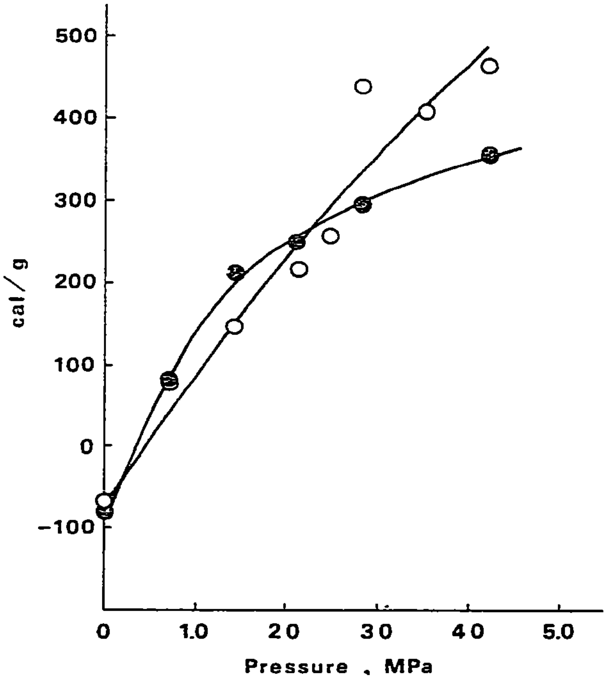


Fig. 3. Variation of decomposition heats of CT in nitrogen or air with pressure. Heating rate: 10°C min^{-1}. ○, N_2; ●, air.

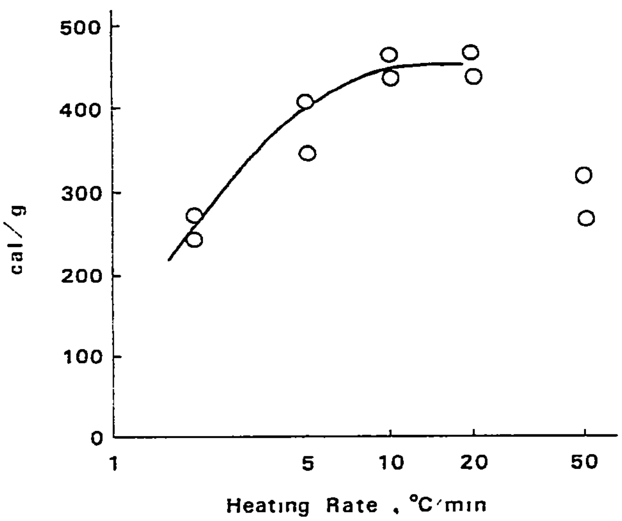


Fig. 4. Influence of heating rates on decomposition heats of CT in nitrogen at 4.23 MPa.

original sample mass in Fig. 3. At pressures less than about 2.6 MPa, the reaction heats of CT in air are somewhat larger than those in nitrogen; this may be due to pronounced thermal oxidation of CT. The decomposition heats in nitrogen, however, had a tendency to increase more than those in air when the pressure was increased above 3 MPa, exhibiting 400—450 cal g^{-1} · The reaction heat by thermal oxidation is proportional to the partial pressure of oxygen, but the oxidation of CT may not proceed well because chlorine in CT will inhibit the oxidation. In general, the degree of weight conversion tends to increase when an explosive decomposition occurs (Fig. 11). It may be necessary to consider the quantities of residue after the reaction when discussing the magnitude of the reaction heat per decomposed mass.

Figure 4 shows an influence of heating rate on the decomposition heat of CT which was allowed to decompose in nitrogen at 4.23 MPa. As shown in Fig. 4, the calorific values of CT increase with increase of heating rate, and

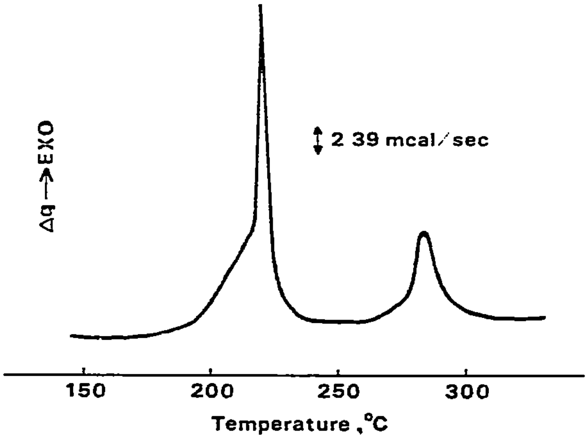


Fig. 5. Pressure DSC curve of CT in nitrogen at 4.23 MPa. Heating rate: 50°C min^{-1}.

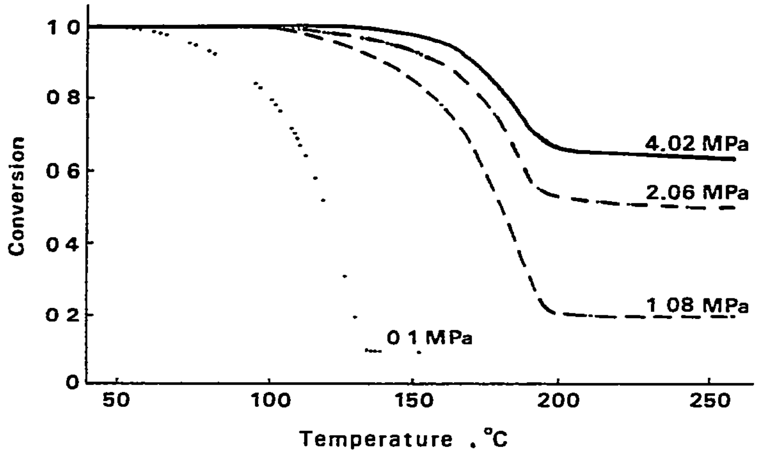


Fig. 6. TG curves of CT in helium at various pressures. Heating rate 10°C min^{-1}, weight $\sim$5 mg.

about 450 cal g^{-1} seems to be a constant value at the heating rate of 10—20°C min^{-1}. The calorific values of CT at 50°C min^{-1} fell to about 300 cal g^{-1}. The pressure DSC curve of CT at that time is shown in Fig. 5. A sharp exothermic peak may exhibit explosive decomposition at about 220°C, and the residue decomposes again with an exothermic reaction at 280°C. When the explosive reaction occurs in the sample cell, there may be appreciable upward leaks of heat flux from the lid of the cell. This seems to be a reason for the decrease of decomposition heat of CT at 50°C min^{-1}.

Pressure TG of CT

Figure 6 shows TG curves of CT in helium at various pressures. The degree of weight conversion is lowered and the decomposition temperatures are

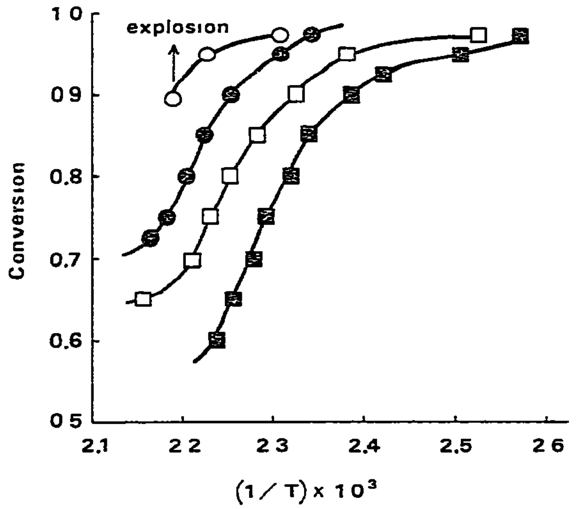


Fig. 7. Variation of TG curves of CT in helium at 4.02 MPa with various heating rates, plotted against the reciprocal of absolute temperature. Weight: $\sim$10 mg. ○, 10°C min^{-1}, ●, 5°C min^{-1}; □, 2.5°C min^{-1}, ▨, 1.25°C min^{-1}.

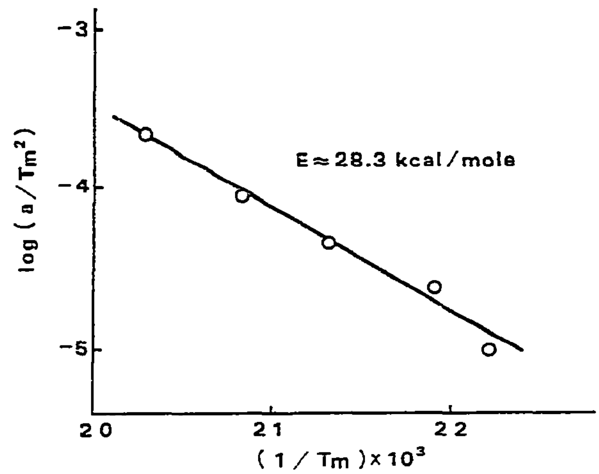


Fig. 8. Kissinger's plots of CT in nitrogen at 4.23 MPa.

shifted to a high temperature range as the ambient pressure is increased. However, CT will scarcely decompose at temperatures above 200° C. CT mostly evaporates at atmospheric pressure between 50—130° C. With an increase in the gas pressure, the evaporation is suppressed and the thermal decomposition may partly proceed at the same time. At 4.23 MPa, only 40% of CT decomposes, leaving a large amount of carbonaceous residue. An explosive decomposition, however, readily occurred in the formation process of the heat-stable substances when the sample weight or the heating rate was increased.

The pressure TG curves of CT (~10 mg), which were allowed to decompose in helium at 4.02 MPa with various heating rates, are shown against the reciprocal of the absolute temperature in Fig. 7. The weight of residue tends to increase as the heating rate is increased, and an explosive decomposition is exhibited at 10° C min^{-1}. CT in helium at 4.02 MPa seems to decompose following a simple reaction mechanism within about 30% of the decomposing material because the TG curves mostly superpose by lateral shifts [5]. This tendency will not be obtained under low pressure gas atmospheres because evaporation may occur at the same time.

The activation energy of CT in helium at 4.02 MPa, about 22.3 kcal mole^{-1}, was obtained from the relation

$$\log a + 0.4567\,(E/RT) = k$$

where a is the heating rate, E is the activation energy, and k is a constant [5]. On the other hand, it is expected that an extrapolated exothermic onset-temperature in a DSC curve corresponds most closely to a DTA peak temperature. It is also possible to calculate the activation energy for the decomposing material by the relation

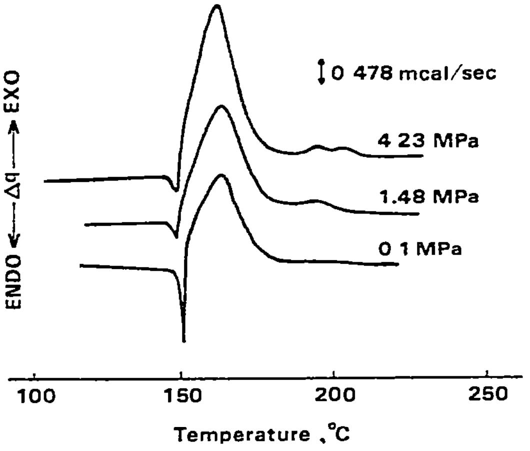
$$d(\ln a/T_{\text{m}}^2)/d(1/T_{\text{m}}) = -E/R$$

where T_{m} is the peak temperature in DTA [6]. Figure 8 shows the Kissinger plots for CT in nitrogen at 4.23 MPa at various heating rates. An activation energy of 28.3 kcal mole^{-1} is relatively close to that obtained from the pressure TG curves, and the frequency factor was calculated to be 7.3×10^{12} min^{-1}, assuming the reaction order to be 1.

Decomposition of AT

Figure 9 shows pressure DSC curves of AT in air at various pressures. The decomposition of AT proceeds exothermally soon after melting at 150°C in spite of the pressure of air or nitrogen. Appreciable differences in the shape of the DSC curves in air and in nitrogen were not observed, but the exotherms in air became larger and the small second exotherms appeared at around 200°C as the pressure was increased. The calorific values of AT in air and nitrogen are plotted against pressure in Fig. 10. As shown, the decomposition heats in nitrogen are slightly affected by the surrounding gas pressure, ranging from 300 to 400 cal g^{-1}. AT, however, was greatly influenced in the decomposition heats by air pressure. The evolution heat in air at 0.1 MPa was about 300 cal g^{-1}, while the air pressure at 1.5—4.0 MPa increased the value to 600—700 cal g^{-1}. From pressure TG of AT, the extent of weight decrease in air was less than that in pressurized helium. Therefore, the oxidation heat of AT is assumed to be much greater than the decomposition heat in inert gas atmospheres.

The pressure TG curves of AT in helium show a complicated pattern as shown in Fig. 11, when about 5 mg of sample were heated at various heating rates. Two stages in the decomposition were observed, with large quantities of residue, when treated at low heating rates. At 10°C min^{-1} an explosive decomposition occurred at 150°C with a temperature rise of about 70°C in the sample, and about 60% instant weight decrease. A complicated reaction mechanism was assumed for the decomposition of AT in helium or air at the pressurized gas atmospheres. This tendency was also confirmed in the TG curves in helium at 0.1 MPa, as shown in Fig. 12. Hence, it may not be possible to derive the kinetic constants from these data.



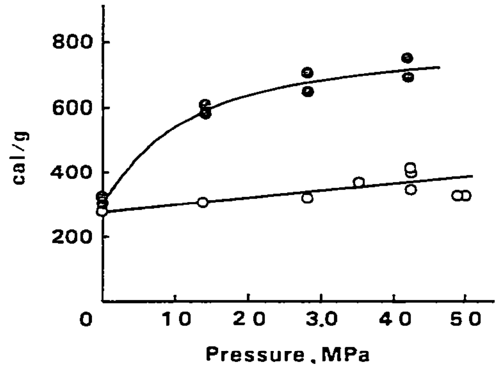
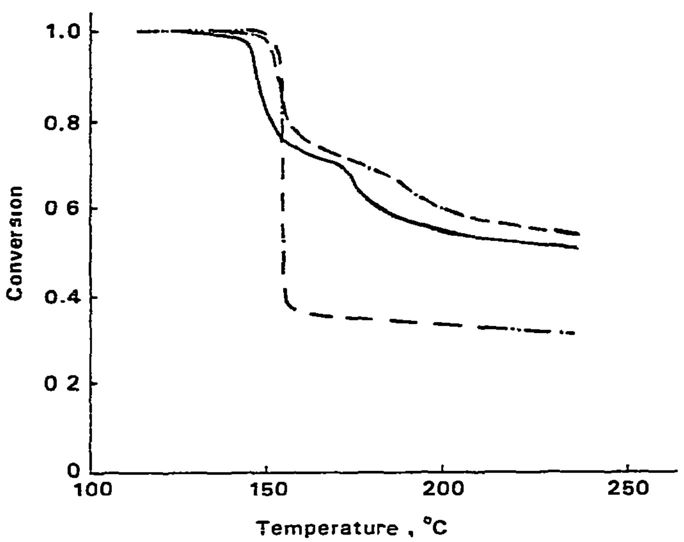


Fig. 9. DSC curves of AT in air at various pressures. Heating rate: 10°C min^{-1}.

Fig. 10. Variation of decomposition heats of AT in nitrogen or air with increase of pressure. Heating rate: 10°C min^{-1}. ○, N_2; ●, air.



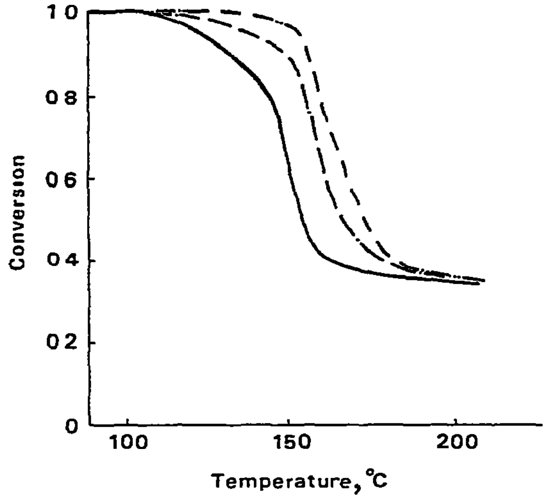


Fig. 11. TG curves of AT in helium at 2.06 MPa at various heating rates. Weight · ~5 mg. ———, 2.5°C min^{-1}; · — · — ·, 5°C min^{-1}; — · · —, 10°C min^{-1}.

Fig. 12. TG curves of AT in helium at 0.1 MPa at various heating rates. Weight ~5 mg ———, 2.5°C min^{-1}; · — · — ·, 5°C min^{-1}; — · · — 10°C min^{-1}.

Decomposition of AAT

Pressure DSC curves of AAT in nitrogen at various pressures are shown in Fig. 13. They show gentle exothermic traces in the temperature range 220—270°C even at gas pressures >1 atm, exhibiting small differences in the areas under the curves. The decomposition heats of AAT in nitrogen ranged from 140 to 180 cal g^{-1} inspite of the increase in pressure. The evolution heats in air had a tendency to slightly increase, but clear DSC curves were not obtained. Although a simple decomposition mechanism was anticipated from the DSC curves in nitrogen, it was confirmed by pressure TG curves. Figure 14 shows the pressure TG curves of AAT in helium at 2.06 MPa at a number of heating rates. The isomorphous sigmoid curves were obtained by plotting the degree of weight conversion against the reciprocal of absolute

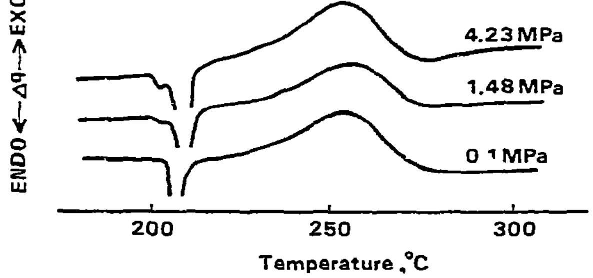
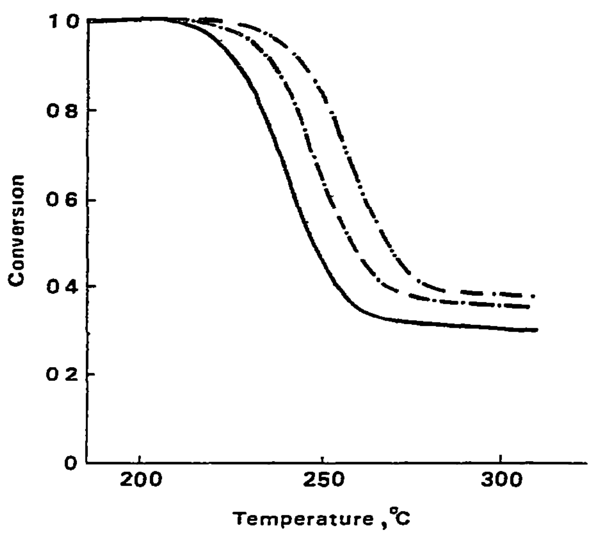


Fig. 13. DSC curves of AAT in nitrogen at various pressures. Heating rate: 10°C min^{-1}.



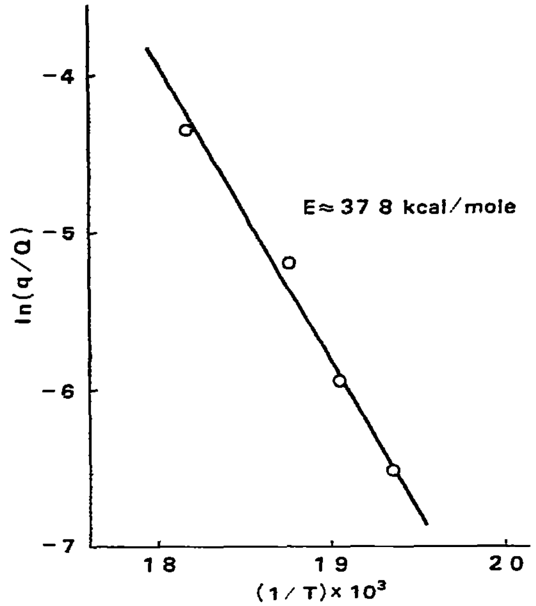


Fig. 14. TG curves of AAT in helium at 2.06 MPa at various heating rates. Weight ~5 mg. ———, 2.5°C min^{-1}, - — · — ·. 5°C min^{-1}; — · · —, 10°C min^{-1}.

Fig. 15. Plots of reaction rates of AAT in nitrogen at 4.23 MPa vs. the reciprocal of absolute temperatures.

temperature. The activation energy was calculated as 37.0 kcal mole^{-1} from Ozawa plots, while 33.5 kcal mole^{-1} was obtained from the TG curves of AAT in helium at atmospheric pressure using the same method.

On the other hand it is also possible to calculate an activation energy from DSC traces using the relation $\ln(q/Q)$ and $1/T$ at a number of heating rates, where q is the rate of enthalpy change at temperature T, and Q is the total amount of reaction heat. An activation energy of AAT in nitrogen at 4.23 MPa was calculated from the slope in Fig. 15 as 37.8 kcal mole^{-1}. From these results, AAT is a thermally stable chemical and possibly decomposes with a simple mechanism, irrespective of the surrounding gas pressure.

CONCLUSION

The thermal stability of three kinds of thiadiazole compounds was investigated using pressure DSC and TG methods. Many factors, such as the presence of an exotherm, the possibility of an explosion, the decomposition heat, and the ignition temperature, are necessary for evaluating the thermal hazard of chemicals. Thermal analysis may be a simple and convenient technique for measuring these factors and the kinetic constants are also obtained. But some chemicals such as CT evaporate or sublimate when heated at atmospheric pressure. Therefore, it may be desirable to evaluate the thermal hazard under gas pressures >1 atm. Pressure DSC, DTA, or TG may be one of the effective methods. The thermal analysis methods, however, may have some disadvantages for the evaluation of chemicals. For example, an appreciable decrease in the calorific value was noticed in the DSC experiments for the explosive decomposition of CT. The other calorific measurements may be necessary for an accurate determination of the decomposition heat.

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