

DIFFERENTIAL THERMAL ANALYSIS AND THERMOGRAVIMETRY OF AMMONIUM PERCHLORATE AT PRESSURES UP TO 51 ATM

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ABSTRACT

The thermal decomposition of pure ammonium perchlorate (AP) was investigated in various gaseous atmospheres at pressures up to 51 atm, using a technique of thermal analysis. It is concluded that the first and second stage decompositions of AP in an atmosphere of oxygen or nitrogen are appreciably accelerated as the pressure is increased. Platinum has a catalytic effect in the high-temperature decomposition and suppresses the sublimation of AP at high temperature ranges in helium atmosphere even at 1 atm. The reaction heat for the high-temperature decomposition of AP in the platinum cell was calculated from the peak temperatures of DTA curves at various pressures to be $77.9 \text{ kcal mol}^{-1}$. The activation energies of the sublimation in helium at 1 atm and of the high-temperature decomposition in the platinum cell at various pressures of helium have also been obtained, giving similar values of 23-25 kcal mol^{-1} .

INTRODUCTION

The decomposition of ammonium perchlorate (AP) has been studied intensively during the past few decades because of the use of AP in rocket-propellant compositions.

It is widely recognized that there are three processes in the thermal decomposition of AP: these processes are low-temperature decomposition, sublimation, and high-temperature decomposition. Jacobs and Russell-Jones¹ explain these processes in terms of proton transfer yielding adsorbed ammonia and perchloric acid. They² also suggest that these molecules of ammonia and perchloric acid can either react together (the low-temperature decomposition) or evaporate into the gas phase; where they either diffuse away from the decomposing AP (sublimation) or undergo further reactions followed by oxidation of ammonia (the high-temperature decomposition).

The burning mechanism and characteristics of AP at high pressures have been the subjects of a large number of investigations³. It seems that the thermal decomposition of AP plays an important role in the burning. The thermal decomposition of AP on the basis of DTA and TG at the ambient pressures of ≤ 1 atm has been shown in several papers⁴⁻⁷.

The aim of the present work is to investigate the effect of enclosure pressure of helium, oxygen, and nitrogen on the thermal decomposition of AP, by use of a high pressure thermobalance and differential thermal analyser.

EXPERIMENTAL

Material

AP used was recrystallized three times with distilled water. The particle size of AP was 50–370 μ (mean: 280 μ).

Apparatus

The high pressure thermobalance and differential thermal analyser, developed at Rigaku Denki Co., Tokyo, are capable of operation in the pressure range from 1 to 51 atm (maximum pressure of 120 atm for the DTA). An oxygen or inert gas atmosphere can be employed in the temperature range from room temperature to 600°C for both apparatus. A sample mass of 2–500 mg is available for the thermobalance.

The schematic diagrams of the apparatus are shown in Figs. 1 and 2. Various types of high pressure thermobalance and differential thermal analyser have been constructed so far^{8–17}. The thermobalance used herein consists basically of a Rigaku Denki electric thermobalance mounted in a pressure vessel. A long sample rod is fitted in the balance to eliminate heat conduction from the furnace. A pressure increase of about 4% of predetermined pressure is observed in the thermobalance at a temperature of 600°C, while for the DTA measurements the pressure increased by heating is released through the control valves. Platinel (\pm) thermocouples are put into contact with shallow platinum pans to measure the sample temperature for both apparatus.

Techniques

An aluminum or platinum cell (5 mm diam., 2.5 mm depth) containing AP (loose powder) of 11–15 mg was laid on the pan for the DTA and TG measurements. Five heating rates ($\sim 1.25, 2.5, 5, 10,$ and $20^\circ\text{C min}^{-1}$) were employed for the experiments in helium, and 5°C min^{-1} in oxygen or nitrogen. Flushing of the apparatus to remove air was accomplished by charging the apparatus with a desired gas at 11 atm and relieving the pressure to atmospheric three times before the measurements were taken. Mass-loss curves of the samples were recorded at a full scale of 20 mg.

Buoyancy effect of thermobalance

While the change in sample mass due to the gas buoyancy is observed in using this thermobalance as the pressure is increased, the two arms of the thermobalance may be balanced at a fixed pressure by the operation of a feedback coil. The apparent mass-loss curves are fully obtained at desired positions on a recorder if a balance weight is suitable.

The correction of the buoyancy effect, therefore, will be accomplished by considering the effects of temperature change and of volume change of sample during the heating. In Fig. 3, the mass-change due to the buoyancy effects of temperature and heating-rate change can be seen as a function of temperature at a fixed pressure of 51 atm of helium, with the buoyancy effect of α -alumina which has almost the same volume as that of AP studied for the TG. The buoyancy effects are pronounced as the gas pressure is increased or the heating rate is decreased. It seems that there is a linear relation between the temperature and the mass-change in the temperature range of 250–500°C.

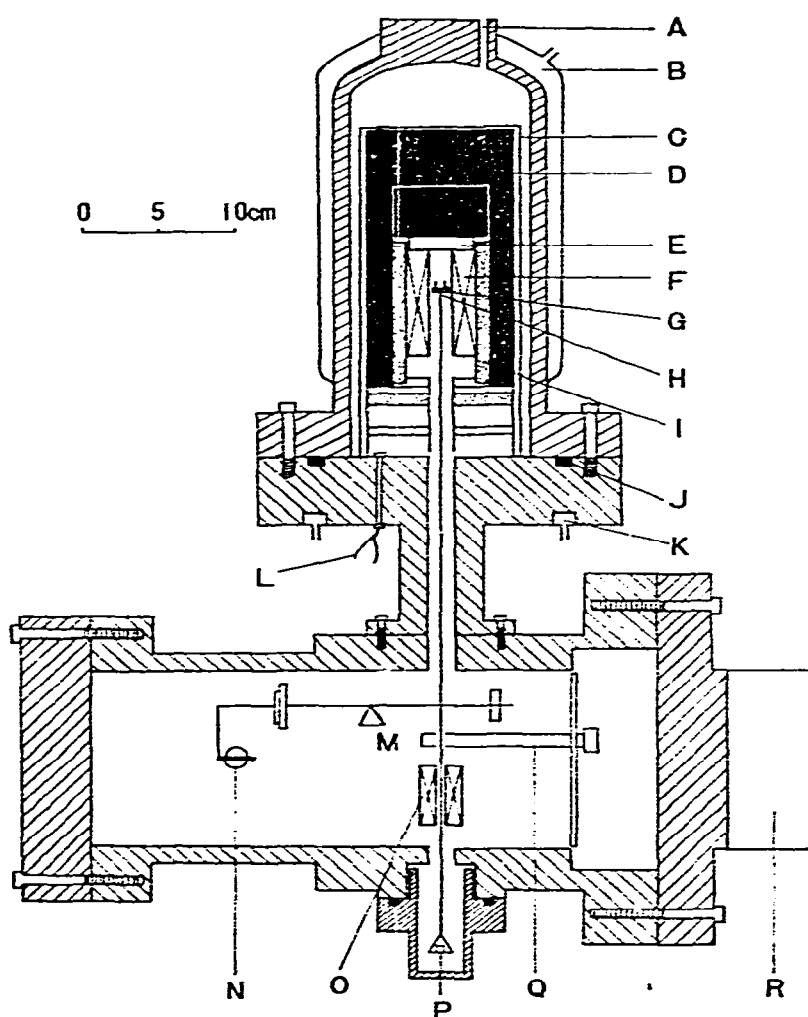


Fig. 1. Schematic diagram of the high pressure thermobalance, A, gas outlet; B, water jacket; C, stainless-steel cover; D, fire-brick; E, quartz glass disk; F, furnace; G, sample pan and cell; H, thermocouple and sample rod; I, glass wool; J, Viton O-ring; K, ditch for water circulation; L, lead wires of thermocouple and furnace heater; M, balance; N, detector of light-quantity; O, feedback coil; P, balance weight; Q, stopper; R, connector of cables for mass-loss detection.

0 1 2 3 cm

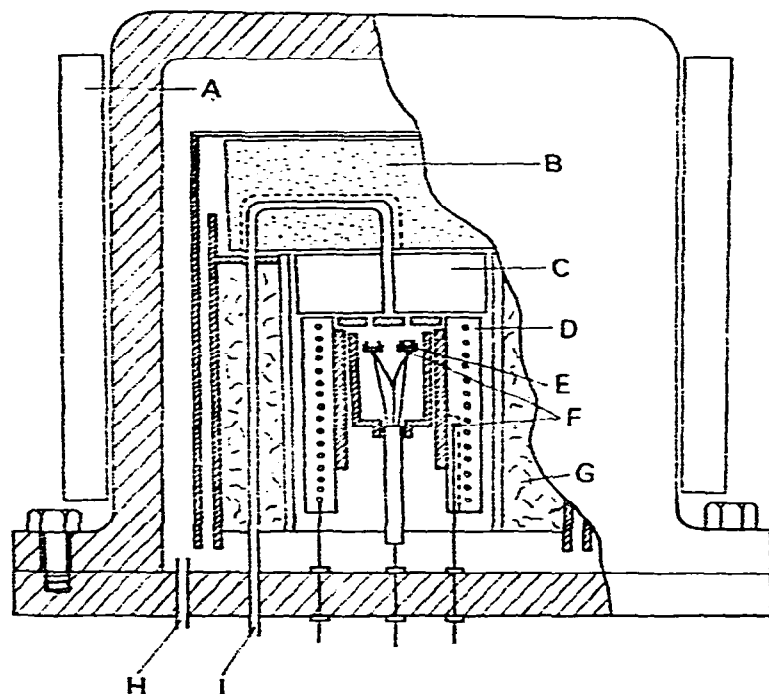


Fig. 2. Schematic diagram of the high pressure differential thermal analyser. A, water jacket; B, firebrick; C, quartz glass disk; D, heater; E, sample pan and cell; F, thermocouples for sample and furnace heater; G, glass wool; H, gas inlet; I, gas outlet.

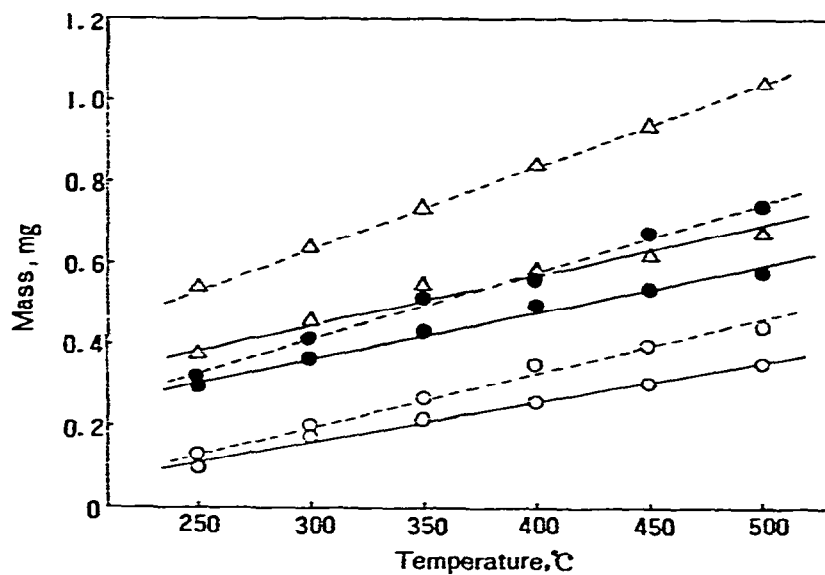


Fig. 3. Apparent mass-increase versus temperature in He of 51 atm at various heating rates. Straight line, blank run; dotted line, run with α -Al₂O₃ of 17.69 mg. (○) 20°C min⁻¹; (●) 5°C min⁻¹; (△) 2.5°C min⁻¹.

The volume change of sample is thought to be proportional to the mass-loss of sample if the density of surrounding gas is assumed to be unchanged in the course of the decomposition of sample. Thus, the corrected curve is obtained by subtracting the buoyancy curve of α -alumina from the original curve, and allotting proportionally the differences of mass-change between the buoyancy curves of α -alumina and of blank run to the revised curve. The effect of the volume change of sample may be neglected when the surrounding gas has a large molecular weight such as oxygen or nitrogen.

RESULTS AND DISCUSSION

DTA in helium

The results of DTA of AP decomposed in the aluminum cell at a heating rate of $5^{\circ}\text{C min}^{-1}$ are shown in Fig. 4 with the various enclosure pressures of helium. The first exotherm at $300\text{--}350^{\circ}\text{C}$, which probably corresponds to the low-temperature

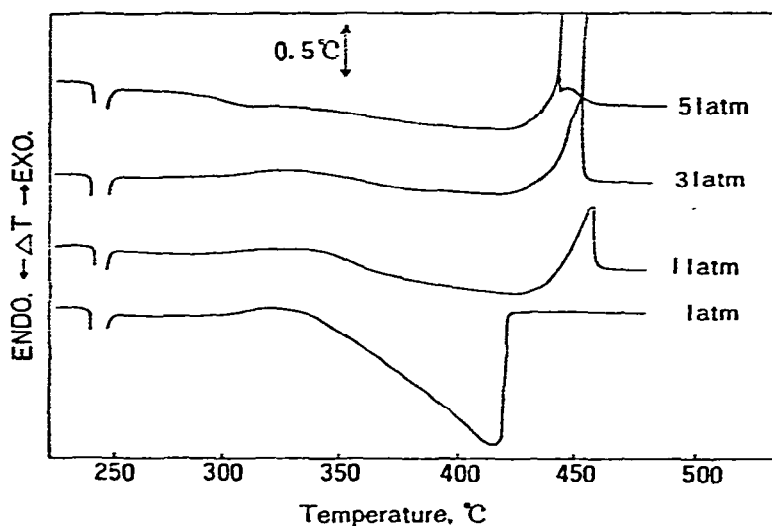


Fig. 4. DTA curves of ammonium perchlorate decomposed (in Al cell) in He at various enclosure pressures. Heating rate, $5^{\circ}\text{C min}^{-1}$.

decomposition of AP, is little affected by the gas pressure and the heating rate. The endothermic peaks at the high pressures may be attributed by the sublimation and the high-temperature decomposition of AP, while the peak at 1 atm is mostly due to the sublimation. The second exothermic reaction leading to deflagration may be understood on the basis of the heat balance between the endothermic reaction of sublimation and the exothermic gas-phase reaction of the high-temperature decomposition of AP. The deflagration is favoured with increase of the gas pressure and the heating rate.

Figure 5 shows the DTA curves of AP decomposed in the platinum cell under the same conditions as those in the aluminum cell. An exothermic peak with a dis-

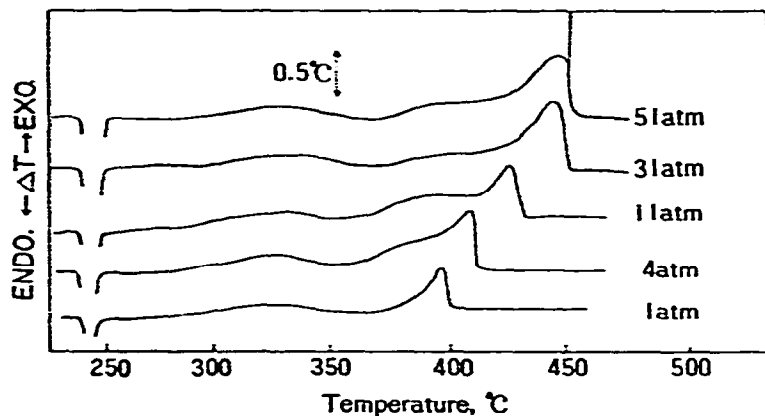


Fig. 5. DTA curves of ammonium perchlorate decomposed (in Pt cell) in He at various enclosure pressures. Heating rate, $5^{\circ}\text{C min}^{-1}$.

cernible shoulder can be seen in the high temperature ranges at the various pressures of helium, with the first exotherm at $270\text{--}350^{\circ}\text{C}$. The figure also shows that the temperature ranges of the second exothermic reaction are increased as the gas pressure is increased, and that only the high-temperature decomposition seems to occur in the high temperature ranges even at an atmospheric pressure. The reaction heat for the high-temperature decomposition of AP was calculated from the peak temperatures at the various pressures using Clausius-Clapeyron's equation, being given a value of $77.9\text{ kcal mol}^{-1}$.

AP decomposition has a prominent feature of its susceptibility to catalyst such as metal oxides². Platinum is also appreciated to be susceptible to the AP decomposition at high temperatures, while aluminum seems to have little catalytic effect on the decomposition. The low-temperature reaction, however, is hardly influenced by the existence of platinum catalyst. The second exothermic curve seems to be partly due to the heat of adsorption of the gaseous molecules of ammonia and perchloric acid on the surface of platinum.

TG in helium

In Fig. 6, the curves of derivative thermogravimetry (DTG) for AP decomposed in the aluminum cell are shown for the fixed pressures of helium at a heating rate of $5^{\circ}\text{C min}^{-1}$. As can be seen in the figure, AP decomposes into two stages. No sharp boundary exists¹⁸ between the first and the second stage decompositions at 1 atm although the first stage decomposition becomes distinct as the pressure is increased. The increasing pressure tends to increase the temperatures of the first and the second stage decompositions, but it is not obvious in the high-temperature ranges at the pressures over 31 atm because the high-temperature reaction of AP becomes dominant rather than the sublimation in these temperature ranges.

The results of TG of AP in helium at 1 and 31 atm at various heating rates are plotted against the reciprocal absolute temperature in Figs. 7 and 8. The figures show

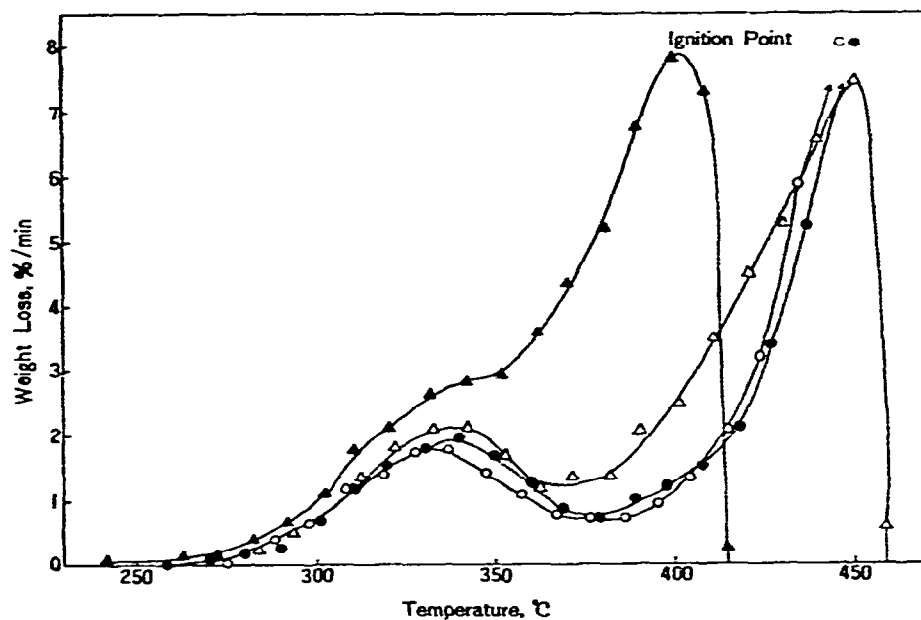


Fig. 6. DTG curves of ammonium perchlorate decomposed (in Al cell) at various pressures of He Heating rate, $5^{\circ}\text{C min}^{-1}$. (O) 51 atm; (●) 31 atm; (Δ) 11 atm; (\blacktriangle) 1 atm.

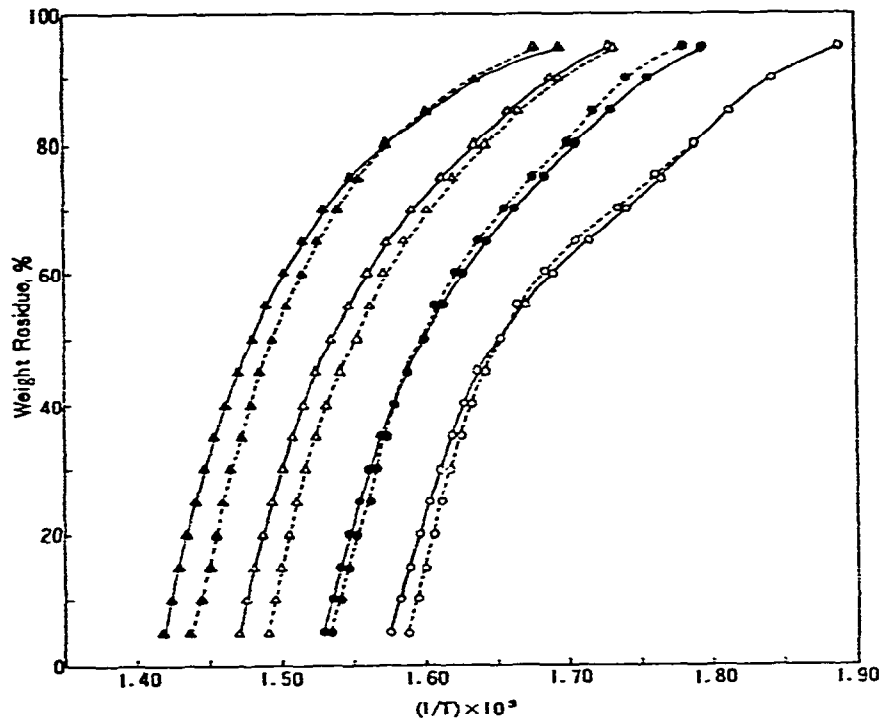


Fig. 7. TG curves for ammonium perchlorate decomposed in Al cell (—) and in Pt cell (---) at 1 atm He at various heating rates, plotted against the reciprocal absolute temperature. (O) $1.25^{\circ}\text{C min}^{-1}$; (●) $2.5^{\circ}\text{C min}^{-1}$; (Δ) $5^{\circ}\text{C min}^{-1}$; (\blacktriangle) $10^{\circ}\text{C min}^{-1}$.

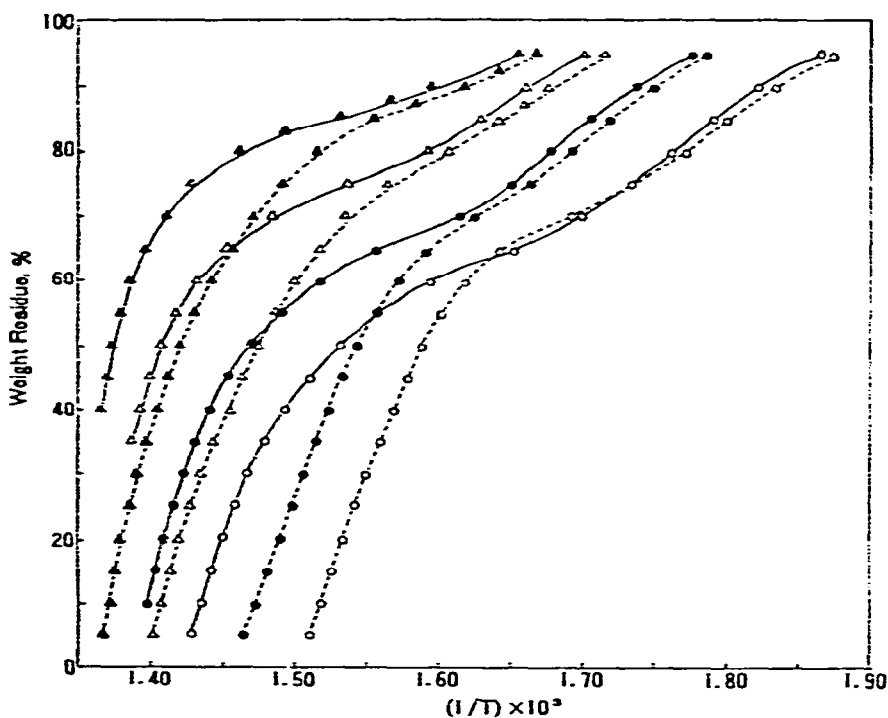


Fig. 8. TG curves for ammonium perchlorate decomposed in Al cell (—) and in Pt cell (---) at 31 atm He at various heating rates, plotted against the reciprocal absolute temperature. (O) 1.25°C min⁻¹; (●) 2.5°C min⁻¹; (Δ) 5°C min⁻¹; (▲) 10°C min⁻¹.

that the decomposition of AP is greatly affected by the gas pressure in the second stage, while it is not so much influenced in the first stage. There is a great difference in the TG between the AP decompositions in the aluminum and platinum cell, especially at the high pressures in the high-temperature ranges. The decomposition of AP at low temperatures is not greatly influenced by platinum catalysis even at high gas pressures.

Ozawa¹⁹ proposed that the properties of the sample are dependent only on the structural quantity of the sample in order to estimate the kinetic parameters with the thermal analysis, and derived an equation of $\int_0^x dx/g(x) = (A/a) \int_0^T \exp(-\Delta E/RT) dT$, where $g(x)$ is the function of a structural quantity, x ; A the frequency factor; a the heating rate; ΔE the activation energy, R the gas constant; and T the absolute temperature. From this equation, TG curves versus the reciprocal absolute temperature at different heating rates can be superposed upon each other by lateral shifts if the weight change is governed by only one activation energy.

Irrespective of the gas pressures of helium, the TG curves of AP decomposed in the platinum cell may be superposed upon each other after the residual weight is approximately less than 60%. The curves for the aluminum cell become difficult to be superposed as the pressure is increased, while the curve at 1 atm can nearly be superposed after the residual weight is also less than ~60%. Superposition is not possible

in cases when the sample decomposes at low temperature ranges (Figs. 7 and 8). Bircumshaw and Newman^{20,21} observed that, below 300°C, AP decomposes to the extent of about 30% at an ambient pressure of 1 atm, decomposition then ceasing at that point.

From the above TG results, it may be thought that, for the AP decomposition in the low-temperature ranges, the transition to the gas phase and the low-temperature reaction of ammonia and perchloric acid will take place simultaneously in helium at the various pressures. The decomposition of AP in the platinum cell in the high-temperature ranges may be due only to the high-temperature decomposition of the gas-phase reactions of these molecules, while the decomposition in the aluminum cell proceeds with the two reactions of the sublimation and the high-temperature decomposition in helium atmosphere at pressures over 1 atm. Platinum is assumed to have a contact catalysis, and the molecules of ammonia and perchloric acid diffused in the gas phase are adsorbed on the surface of the platinum cell. Thus, the oxidation of ammonia in the presence of platinum by perchloric acid takes place easily at relatively low temperatures at the second stage of AP decomposition.

Activation energy

The activation energy for sublimation of AP is thought³ to be close to half the enthalpy of sublimation, calculated to be 29.2 kcal mol⁻¹ by Pearson²² and to be around 30 kcal mol⁻¹ at 1 atm pressure by Jacobs and Russell-Jones¹. Bircumshaw and Phillips²³ indicated an energy of activation for sublimation of 21 kcal mol⁻¹ under low pressures. There is a considerable variation in the literature values³ for the activation energy of the low-temperature decomposition of AP, lying between 17 to 41 kcal mol⁻¹. The activation energy for the high-temperature decomposition³ at pressures ≤ 1 atm is varied mostly from 23 to 46 kcal mol⁻¹. Jacobs and Russell-Jones^{1,2} found, however, that the activation energies for sublimation, low-temperature decomposition, and high-temperature decomposition all have the same values of ~30 kcal mol⁻¹.

The "Ozawa plots"¹⁹ were taken for the determination of the activation energy of the decomposing AP as shown in Fig. 9, in which the activation energy may be calculated from the slopes of these linear plots. The slopes have mostly the same values for the AP decomposition in the platinum cell at the various pressures after the decomposition of about 40% of the total amount. However, the AP decomposition in the aluminum cell at the high temperature regions does not represent the same slopes as the pressure is increased, although it shows almost the same slopes at a pressure of 1 atm.

The activation energy thus obtained for the sublimation of AP, decomposed in the aluminum cell in helium at 1 atm, was 23.6 kcal mol⁻¹. The activation energies for the gas-phase reactions of ammonia and perchloric acid in the presence of platinum were 24.9 kcal mol⁻¹ at 1 atm, 25.6 kcal mol⁻¹ at 11 atm, 24.9 kcal mol⁻¹ at 31 atm, and 23.2 kcal mol⁻¹ at 51 atm. In these calculations, the activation

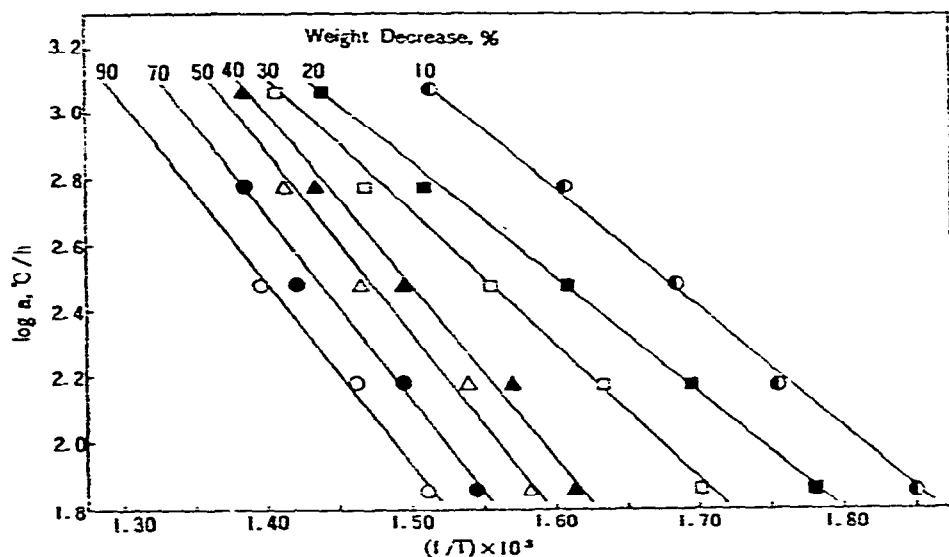


Fig. 9. Plots of the logarithm of heating rate versus the reciprocal absolute temperature for ammonium perchlorate decomposition (in Pt cell) at 51 atm He.

energies were obtained for each 5% decrease of the decomposition at the high-temperature ranges and averaged among them. It may not be possible to determine the activation energies from the Ozawa plots for the decomposition at the low-temperature ranges and for the decomposition in the aluminum cell at the high-temperature ranges, because the two or more processes of reaction are included in these decompositions.

DTA and TG in oxygen or nitrogen

The DTG curves for AP decomposed in the aluminum cell in the various atmospheres at 1 and 51 atm are presented in Figs. 10 and 11. AP also decomposes into two stages in the atmospheres of oxygen and nitrogen, and this break becomes distinct as the gas pressure is increased.

Products from the thermal decomposition of AP have been shown in many papers^{20,24,25}. It was revealed in these data that oxygen, hydrogen chloride, nitrous oxide, and chlorine were obtained in quantity with small amounts of nitric acid, nitrogen dioxide, and nitrogen, at decomposition temperatures ranging from 180 to 380°C. The ratio of O₂ to N₂ fluctuated between around 4:1 and 10:1. If O₂ is one of the main products, AP decomposition may be affected by an oxygen atmosphere of high pressure. There are little differences in the first stage decompositions in the various gas atmospheres at 1 atm, but the second stage decompositions at 1 atm relating to the sublimation of AP have a tendency to be suppressed by the presence O₂ or N₂. However, O₂ and N₂ promote the first and second stage reactions remarkably with increase of the pressure, showing little differences in the decompositions in O₂ and N₂ atmosphere.

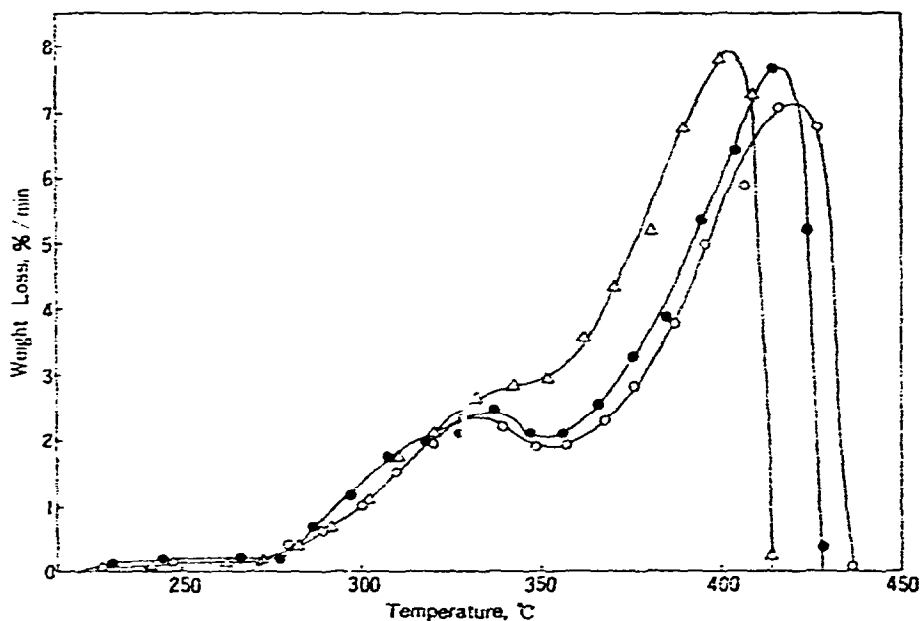


Fig. 10. Effect of O₂ or N₂ at 1 atm on the thermal decomposition of ammonium perchlorate in Al cell. Heating rate, 5°C min⁻¹. (O) N₂; (●) O₂; (Δ) He.

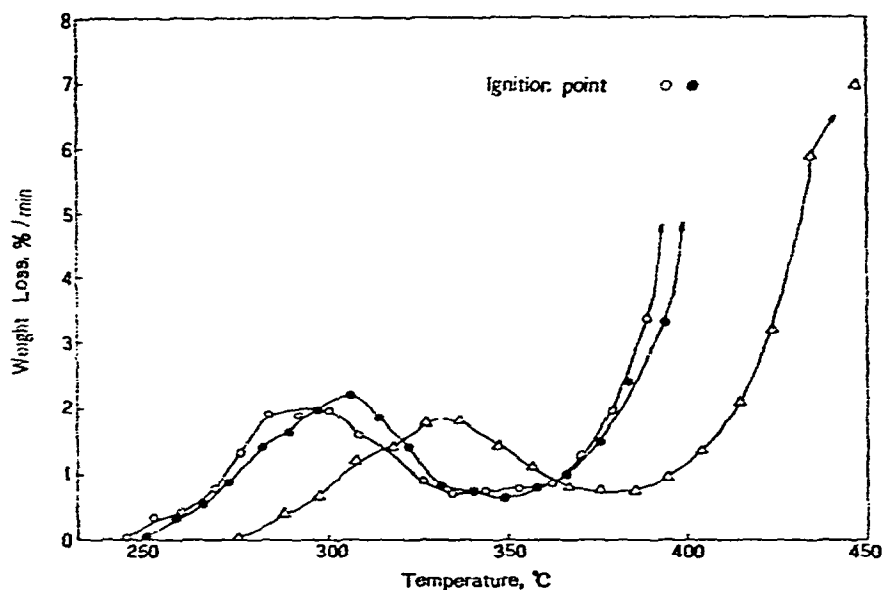


Fig. 11. Effect of O₂ or N₂ at 51 atm on the thermal decomposition of ammonium perchlorate in Al cell. Heating rate: 4.3°C min⁻¹ in O₂ and N₂ atmosphere; 5°C min⁻¹ in He atmosphere. (O) N₂; (●) O₂; (Δ) He.

Figures 12 and 13 show the DTA curves of AP decomposed in the atmospheres of O_2 and N_2 of the various pressures with the aluminum cell (heating rate: $5^\circ C \text{ min}^{-1}$). The similarity of these two figures is of interest in connection with the influence of surrounding gases on AP decomposition. The figures show that larger exothermic peaks are revealed in the first stage reactions in O_2 and N_2 than in He atmospheres (Fig. 4), and these exothermic reactions tend to initiate immediately

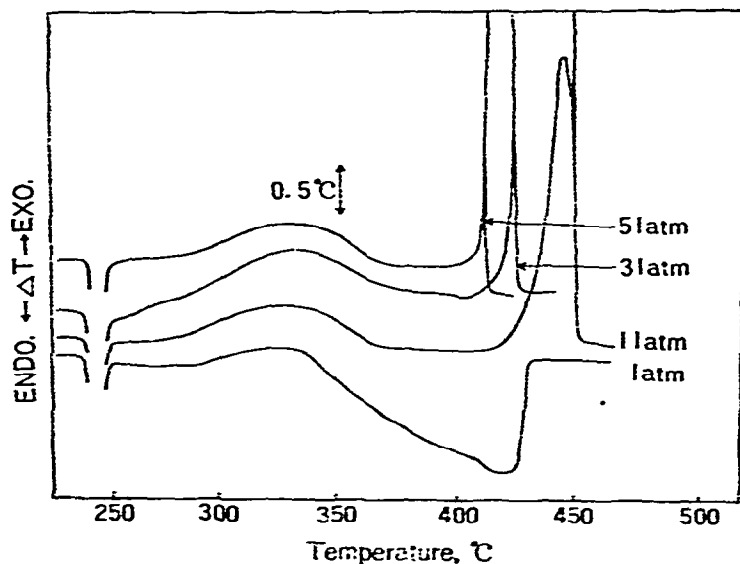


Fig. 12. DTA curves of ammonium perchlorate decomposed (in Al cell) in O_2 at various enclosure pressures. Heating rate, $5^\circ C \text{ min}^{-1}$.

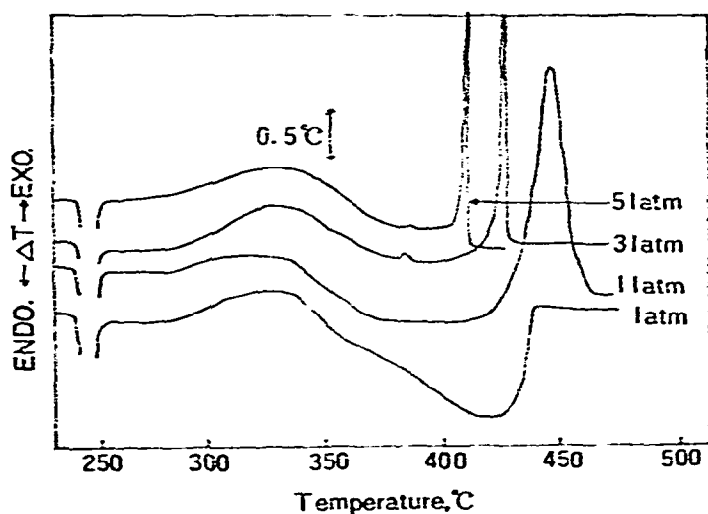


Fig. 13. DTA curves of ammonium perchlorate decomposed (in Al cell) in N_2 at various enclosure pressures. Heating rate, $5^\circ C \text{ min}^{-1}$.

after the crystalline phase transition of AP. The sublimation of AP will also take place at high-temperature ranges in O₂ and N₂ atmospheres of 1 atm, and AP easily deflagrates with increase of the pressure.

It is assumed that the low-temperature decomposition of AP will be enhanced by the pressure of O₂ or N₂, before the molecules of ammonia and perchloric acid diffuse into the gas phase. O₂ or N₂ of high pressure promotes more extensively the gas-phase reactions of these molecules than helium at the high-temperature ranges. These phenomena are not well understood, but these reactions are perhaps related to chemisorption of O₂ or N₂ on the AP surface.

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