

Influence of sample container volume on the thermal decomposition behavior of nitrocellulose/acid mixtures

Satomi Fukui^{*}, Katsumi Katoh^{†**}, Yuka Ogasawara^{**}, Hiroki Matsunaga^{**},
Eiko Higashi^{**}, and Shuhei Kawaguchi^{***}

^{*}Graduate School of Engineering, Fukuoka University, 8-19-1 Nanakuma, Jonan, Fukuoka-shi, Fukuoka, 814-0180 JAPAN

^{**}Faculty of Engineering, Fukuoka University, 8-19-1 Nanakuma, Jonan, Fukuoka-shi, Fukuoka, 814-0180 JAPAN
Phone: +81-92-871-6631

[†]Corresponding author: kkatoh@fukuoka-u.ac.jp

^{***}Taketoyo Plant, NOF Corporation, 61-1 Kitakomatsudani, Taketoyo-cho, Aichi, 470-2379 JAPAN

Received: November 2, 2017 Accepted: August 16, 2018

Abstract

The thermal decomposition behavior of nitrocellulose (NC) and its mixtures with acid solutions (H₂SO₄ or HNO₃) was studied in various sample containers having different internal volumes, using differential scanning calorimetry (DSC) and heat flow calorimetry (C80). The thermal stability of NC and its acid mixtures was evaluated from the decomposition temperature observed by DSC under controlled heating conditions, and the induction time before heat release measured by C80 under isothermal conditions. The thermal stability of NC alone remained unchanged, regardless of the sample container volume. In contrast, the thermal stability of the NC/H₂SO₄ decreased slightly with increasing container volume, suggesting that the solvent water in H₂SO₄ could be easily vaporized in a large-volume or open container and that the H₂SO₄ solution condensed to a greater extent in large containers than in smaller containers. NC/HNO₃ was the most destabilized when an intermediate-volume container was used, although the DSC data were largely scattered even under the same conditions. Assuming that the HNO₃ solution (liquid phase) stabilizes NC by absorbing the reaction heat and that the vaporized HNO₃ shows high reactivity with NC, the sample is the most destabilized in a certain volume of the container by the balance between the concentration of gaseous HNO₃ and the amount of remaining liquid, which is possibly reflected in the experimental results.

Keywords: nitric acid ester, nitrocellulose, spontaneous ignition, DSC, heat flow calorimetry

1. Introduction

Nitrocellulose (NC) is a typical example of nitric acid esters with O-NO₂ bonds. NC is widely used as a starting material for celluloid products, lacquer paints, adhesives, gunpowder etc. It is also a key material of the gas generator for seat belt pretensioners in automobiles. However, NC is a self-reactive material prone to spontaneous ignition. Numerous explosion accidents related to the spontaneous ignition of NC have occurred in storage processes^{1)–9)}.

In general, NC is known to spontaneously ignite even at room temperature by the accumulation of the decomposition heat. The thermal bond scission of O-NO₂ and hydrolysis by atmospheric water vapor have been considered to be responsible for the initial stage of the decomposition^{10,11)}. Hydrolysis is an autocatalytic reaction promoted by the spontaneously generated HNO₃ and residual H₂SO₄ used in the synthetic process. Thus, the reaction between the acid and NC is important from the viewpoint of safety with respect to handling NC, and

several studies on the thermal stability of NC/acid mixtures have been reported^{11)–20)}.

According to the previous studies, the thermal stability varied with the types of acids included in NC. Considering the previous results comprehensively, it can be speculated that H₂SO₄ strongly accelerates the NC thermal decomposition, whereas HCl hardly reacts with NC. As for HNO₃, the reactivity could be largely changed by the test conditions such as the heating rate. In our previous study^{12),13)}, we clarified that HNO₃ could accelerate the NC decomposition to a greater extent than H₂SO₄ in some cases. In addition, the thermal decomposition behavior of NC mixed with an acid could be changed by the type of sample container, such as sealed and open containers. For instance, the thermal decomposition of NC/H₂SO₄ was found to be more accelerated in open containers than in sealed containers, whereas NC/HNO₃ showed the opposite behavior, which suggested that the thermal stability of NC mixed with an acid changes depending on the storage container volume.

In this study, in order to investigate the influence of the sample container volume on the reactivity of NC/acid mixtures, the thermal decomposition behavior of NC alone and its mixture with HNO₃ and H₂SO₄ was measured in various sample containers with different internal volumes by differential scanning calorimetry (DSC)²¹⁾ and heat flow calorimetry (C80)²²⁾.

2. Experimental

2.1 Samples

NC (N% = 12.5) manufactured by NOF Corp. was employed as the test sample after drying for several days under vacuum. Acid solutions added to NC were H₂SO₄ and HNO₃ manufactured by Wako Pure Chemical Industries. These acids were mixed with NC after dilution to 2.3 mol·L⁻¹ with pure water.

2.2 DSC measurements

The diluted H₂SO₄ and HNO₃ solutions (1.25 mg each) were added to NC (5.0 mg) and mixed well by a bamboo skewer in a glass tube. Then, the sample mixtures and NC alone used as the control sample (0.2 mg each) were placed in various containers made of SUS with different internal volumes: an open container (Hitachi High-Tech Science Corp.); and sealed containers with volumes of 15 μL (Hitachi High-Tech Science Corp.) and 50 μL and 100 μL (Swiss Institute for the Promotion of Safety & Security). Each container was placed in the DSC apparatus (DSC 3100 S, Mac Science Co., Ltd.), and the thermal decomposition behavior of each sample was monitored at 0.2, 1, 3, and 5 °C·min⁻¹ heating rates in the temperature range of 20–280 °C. The thermal stability of NC alone and its acid mixtures was evaluated from the obtained DSC thermograms, mainly based on the exothermic peak temperature (T_p).

2.3 C80 measurements

For the C80 measurements (Setaram Instrumentation), 8.0 mg samples of NC alone and its acid mixtures were

used. The mass ratio of NC/acid was the same as that used for the DSC measurements. The sample was loaded into a glass tube, which was then placed in a stainless-steel pressure container made (Rigaku Corp.), as shown in Figure 1. The space volume in the container was adjusted to 1.2, 3.2, and 4.0 mL by filling glass beads (Glass beads BZ-1, 0.991–1.397 mm, AS ONE Corp.) or by changing the size of the internal glass tube. Each container was set in a C80 apparatus, and the thermal decomposition behavior was monitored under isothermal storage at 70 °C. In the C80 measurements, the elapsed time from the beginning of the storage until the peak of heat release is defined as the induction period (t_p) and is used as the index of thermal stability.

3. Results and discussion

3.1 Thermal decomposition behavior of NC alone

The DSC thermograms of NC at a 1 °C·min⁻¹ heating rate are shown in Figure 2. The shape of the thermogram hardly changed, regardless of the container volume, although the amount of heat generated under the open conditions was lower than that under the sealed conditions due to the radiation of heat from the system. Further, as shown in Figure 3, the T_p values hardly changed with the

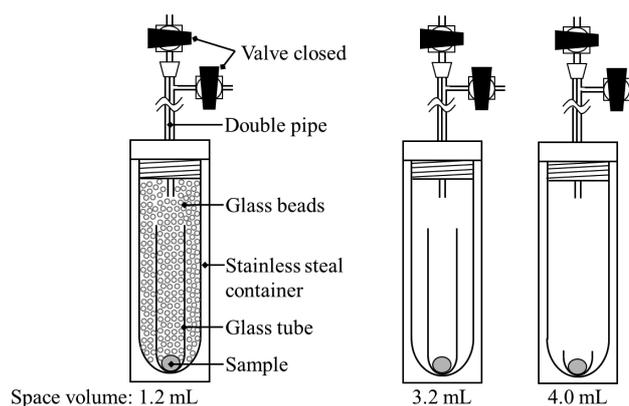


Figure 1 Schematic of the C80 containers.

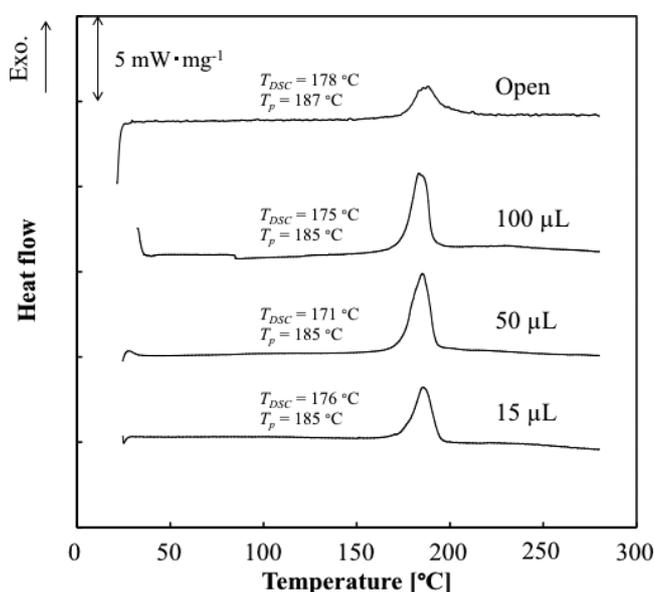


Figure 2 DSC thermograms of NC alone in various sample containers at a heating rate of 1 °C·min⁻¹.

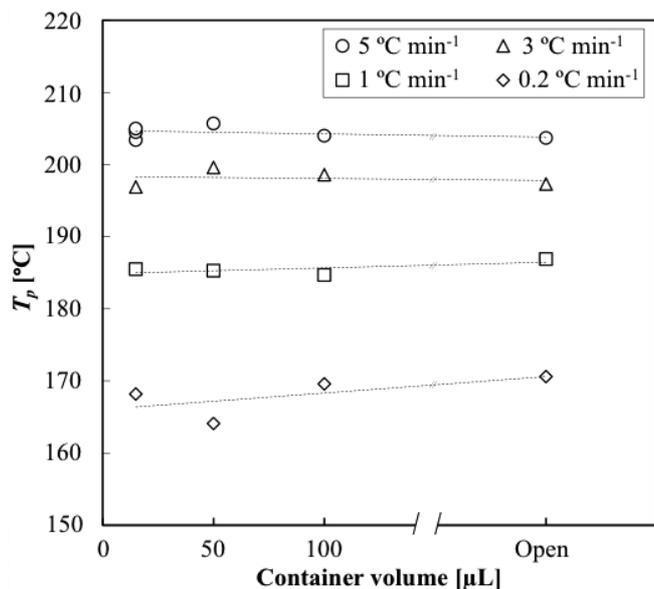


Figure 3 Relationship between the container volume and T_p of NC alone.

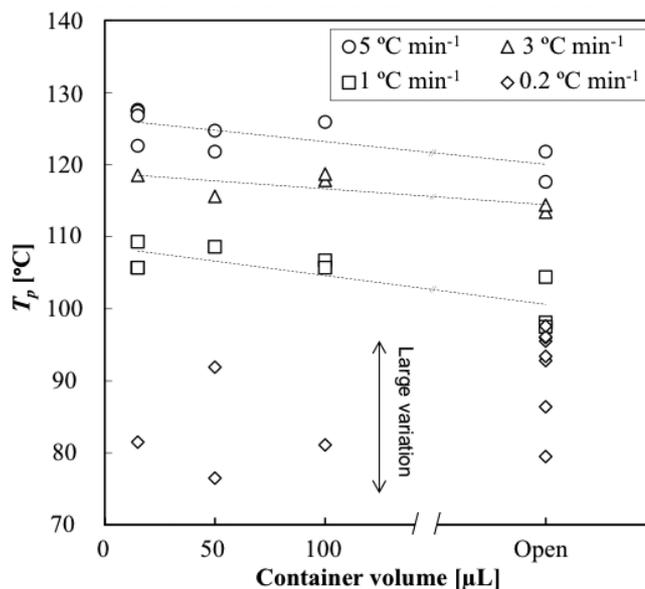


Figure 5 Relationship between the container volume and T_p of NC/H₂SO₄.

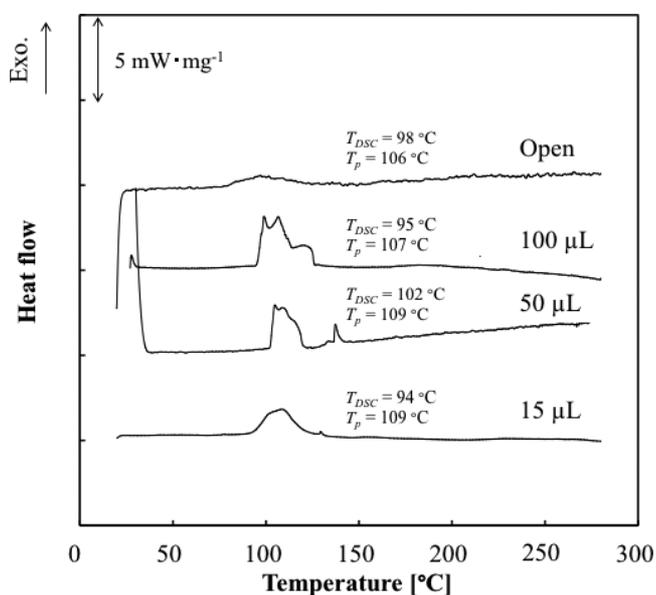


Figure 4 DSC thermograms of NC/H₂SO₄ in various sample containers at a heating rate of 1 °C min⁻¹.

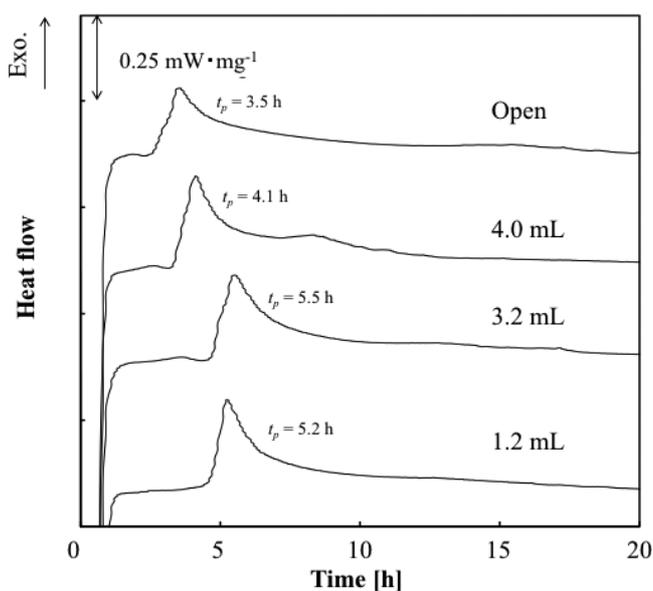


Figure 6 Thermograms of NC/H₂SO₄ measured with a C80 calorimeter at a constant temperature of 70 °C in various sample containers.

difference in the container volume. This aspect was common to different heating rates between 0.2 and 5 °C min⁻¹. Therefore, it is reasonable to consider that the sample container volume hardly influences the thermal stability of NC alone.

C80 measurements under isothermal conditions at 70 °C revealed that NC did not release the reaction heat until at least 40 h for all the sample containers demonstrated in Figure 1.

3.2 Thermal decomposition behavior of NC/H₂SO₄

The DSC thermograms of NC/H₂SO₄ under 1 °C min⁻¹ observed using different container volumes are shown in Figure 4, and the relationship between the container volume and T_p is summarized in Figure 5. The decomposition temperature of NC/H₂SO₄ decreased by approximately 70 °C as compared to that of NC alone, and

multiple reactions were speculated to occur considering the shapes of the thermograms, indicating that H₂SO₄ accelerated the decomposition of NC.

In addition, the data in Figure 5 suggested that the sample container volume influences the thermal decomposition behavior of NC/H₂SO₄; T_p slightly decreased with an increase in the sample container volume although the large variation obscured this tendency under 0.2 °C min⁻¹ of heating rate. A similar tendency was also confirmed when the onset temperature (T_{DSC}) was considered. Furthermore, when the C80 measurements were carried out for NC/H₂SO₄ under isothermal conditions at 70 °C, the exothermic peak appeared within 5 h and t_p was slightly shortened with increasing volume of the space, as shown in Figure 6. This implied that the thermal stability of NC/H₂SO₄ decreased with increasing sample container volume.

This behavior might be related to the fact that the amount of vaporized water in H₂SO₄ aqueous solution varies depending on the container volume. When the NC/H₂SO₄ mixture is heated during the thermal analysis, only water from the added H₂SO₄ solution is vaporized because the vapor pressure of H₂SO₄ is extremely low²³. Thus, the H₂SO₄ solution condenses more in a larger sample container, resulting in increased concentration of the H₂SO₄ solution, and the thermal stability decreases.

In our previous study that compared the thermal decomposition behaviors in sealed and open containers¹³, the difference between the thermal decomposition behaviors due to the airtightness of the sample containers was more significant than that observed in the present study. For example, during C80 measurements under the open conditions, the NC/H₂SO₄ decomposed drastically before the temperature reached 70 °C. In the previous study, a higher concentration of H₂SO₄ solution (6.6 mol L⁻¹) was employed as the additive. This difference most probably affected the experimental results.

3.3 Thermal decomposition behavior of NC/HNO₃

The thermal decomposition behaviors of NC/HNO₃ at 1 °C·min⁻¹ heating rate, and the relationship between T_p and the container volume at each heating rate are shown in Figures 7 and 8. At a low heating rate (0.2 and 1 °C·min⁻¹), T_p of NC/HNO₃ decreased compared to that of NC alone, indicating that the thermal stability of NC decreased in the presence of HNO₃.

Additionally, as shown in Figure 8, T_p increased in the open container at a low heating rate. A similar tendency was observed during the C80 measurements under isothermal storage; the NC/HNO₃ did not release exothermic heat at least for 40 h, as shown in Figure 9, suggesting that NC/HNO₃ stabilized when stored in open containers.

However, the plot in Figure 8 varied notably in comparison with those of NC alone and NC/H₂SO₄

described above. This aspect was particularly enhanced with respect to T_p at 50 μL, and T_p appeared to decrease at 50 μL. In order to confirm whether the fluctuation at 50 μL is simply due to an experimental error, the same DSC measurements were conducted for a different NC sample with N% = 13.4. In this case, T_p was observed to decrease further when the 50 μL container was used, as shown in Figure 8. Moreover, in the C80 measurement results shown in Figure 9, t_p of NC/HNO₃ was most shortened for a sample volume of 3.2 mL. Therefore, NC/HNO₃ might be considered to be most destabilized in containers with a certain volume. Next, in order to compare the results of DSC and C80 measurements, the ratio of the sample container volume and the sample mass ($V \cdot M^{-1}$) was calculated, and the relationships, T_p vs. $V \cdot M^{-1}$ and t_p vs. $V \cdot M^{-1}$ were investigated. As shown in Figure 10, the plots largely fluctuated around $V \cdot M^{-1} = 200\text{--}400 \mu\text{L} \cdot \text{mg}^{-1}$,

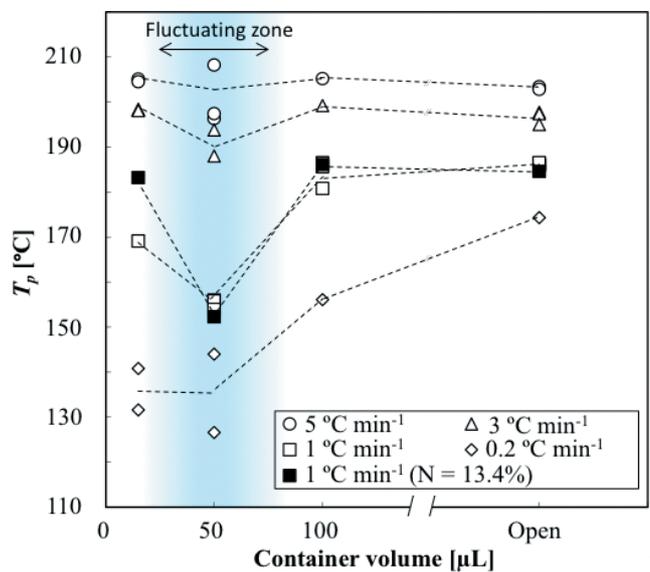


Figure 8 Relationship between the container volume and T_p of NC/HNO₃.

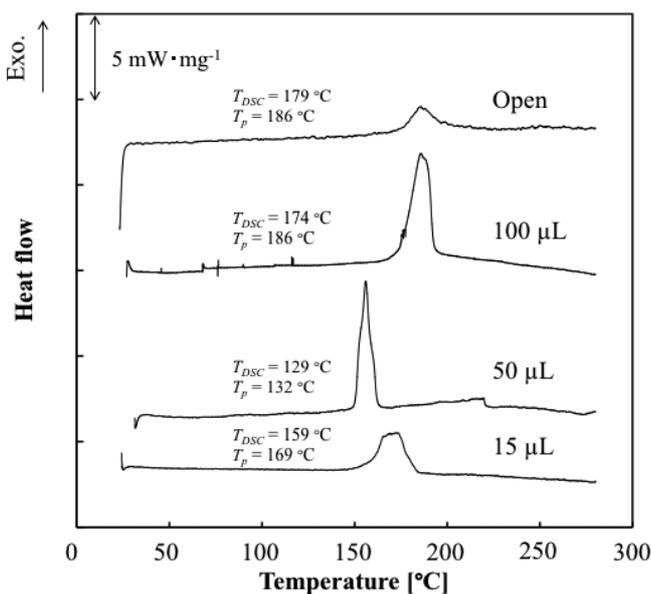


Figure 7 DSC thermograms of NC/HNO₃ in various sample containers at a heating rate of 1 °C·min⁻¹.

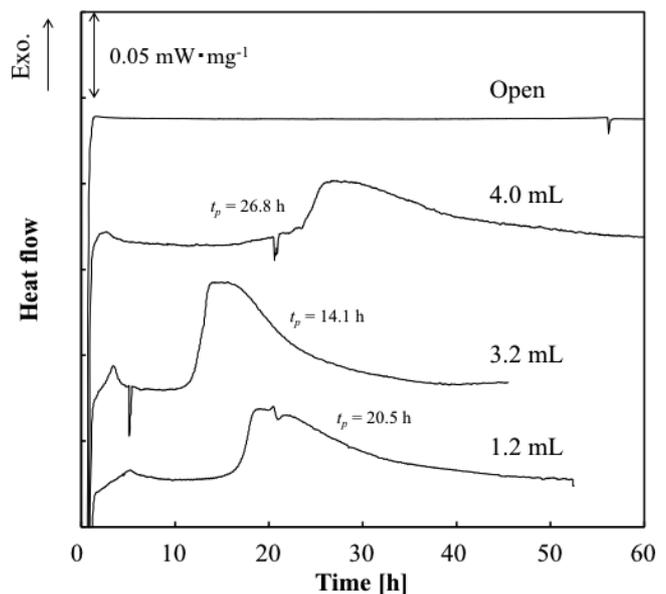


Figure 9 Thermograms of the NC/HNO₃ mixture measured with a C80 calorimeter at a constant temperature of 70 °C in various containers.

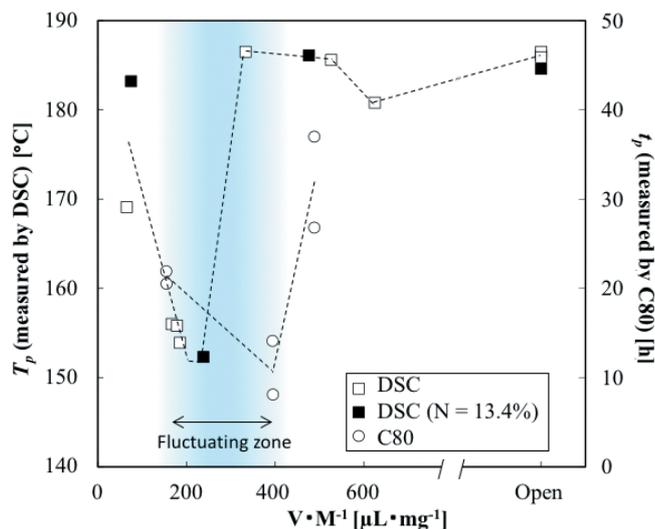


Figure 10 Relationship between $V \cdot M^{-1}$ and T_p of NC/HNO₃.

regardless of the differences between the samples and measurement methods.

In a previous study¹³⁾, the thermal decomposition behaviors of NC/HNO₃ in sealed and open containers were compared, and gaseous HNO₃ was suggested to promote the thermal decomposition of NC rather than liquid HNO₃. Moreover, in the present study, the same gas-solid reactions would occur because NC/HNO₃ is stabilized in open containers. Further, in another study²⁴⁾, it was demonstrated that the thermal decomposition of NC mixed with pure water could be prevented by including more than a specific amount of water, in contrast to the case of dry NC. This result suggested that additives in the liquid phase stabilize NC by absorbing the heat of decomposition.

Based on these previous studies, the thermal stability of NC/HNO₃ is possibly determined by the ratio of the gaseous and liquid HNO₃. That is, when the space volume against the quantity of NC/HNO₃ or added HNO₃, such as $V \cdot M^{-1}$, is excessively small, most of the HNO₃ solution remains in the liquid phase even upon heating, and the liquid HNO₃ and solvent water are thought to prevent the decomposition of NC. On the contrary, when the space volume is large, the decomposition of NC is accelerated because the amount of liquid HNO₃ decreases and that of gaseous HNO₃ or the derived NO_x, which are highly reactive toward NC, increases. Furthermore, when the $V \cdot M^{-1}$ is excessively large, for example, in an open container, the highly volatile HNO₃²⁵⁾ is completely vaporized, and the decomposition behavior becomes the same as that of NC alone. Such an effect possibly leads to the characteristic experimental results of NC/HNO₃, with the least stability observed when $V \cdot M^{-1} = 200\text{--}400 \mu\text{L} \cdot \text{mg}^{-1}$.

4. Conclusion

In this study, we examined the influence of the sample container volume on the thermal decomposition behaviors of NC/acid mixtures, using DSC and C80 calorimetry. The results led to the following conclusions:

- The exothermic peak temperature (T_p) and the

induction time (t_p) of NC alone hardly changed with the container volume, suggesting that the thermal stability of NC alone does not depend on the conditions used.

- In NC/H₂SO₄, T_p and t_p decreased as compared to those of NC alone and slightly decreased with increasing container volume. The thermal decomposition of NC was thought to be promoted in larger containers since the aqueous H₂SO₄ solution added to NC is concentrated due to the evaporation of water.
- T_p and t_p of NC/HNO₃ decreased as compared to those of NC alone. Moreover, T_p and t_p showed a decreasing trend with increasing container volume. In addition, the DSC data largely varied even under the same conditions, but NC/HNO₃ was most destabilized when an intermediate-volume container was used. Provided that liquid HNO₃ stabilizes NC by absorbing the reaction heat and gaseous HNO₃ is highly reactive toward NC, NC/HNO₃ is possibly most destabilized in a certain container volume due to the variation in the balance between the concentration of the gaseous HNO₃ and the amount of remaining liquid.

Acknowledgements

This work was supported by the JSPS KAKENHI Grant-in-Aid for Young Scientists (B) (Grant No. JP 50470042) and financial support from the Central Research Institute of Fukuoka University (Grant No. 147103).

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