

Study on the thermal behavior of nitroglycerine

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Abstract

In order to investigate the heat release behaviors of nitroglycerine (NG), the thermal analysis of NG was performed under the heating condition and the isothermal conditions in various atmospheres. Under the heating condition, two heat releases of NG were observed at approximately 416 K and 436 K in the presence of O₂. The amount of heat release at the lower temperature was dependent on the partial pressure of O₂. In N₂, no heat release was observed around those temperature ranges. Even in a 4 vol. % NO₂ / N₂ atmosphere, no heat release was observed at that temperature. On the other hand, in 4 vol. % NO₂ / air, large heat release was observed at approximately 387 K. Under the isothermal condition, the induction period was shortened in the presence of O₂. The induction period in 4 vol. NO₂ / air was shorter than that in air and the induction period in 4 vol. NO₂ / N₂ was shorter than that in N₂. NO₂ in the presence of O₂ contributed to decomposition of NG more than NO₂ in the absence of O₂.

Keywords: Self ignition, Spontaneous ignition, Nitric ester, Nitric acid ester

1 Introduction

Nitroglycerine (NG) finds a fit in many applications. For instance, NG is a main ingredient of dynamites and smokeless powders such as a double base propellant and as a triple base propellant. And it is used as sublingual tablets for angina and cardiac infarct. However, nitric esters such as NG tend to ignite spontaneously during the storage, which causes the serious accidents. Those accidents which were caused by the spontaneous ignition of nitric ester have been reported even in recent years¹⁾.

Generally, it has been believed that the spontaneous ignition of nitric ester is caused by the reaction between nitric ester and NO₂^{2), 3)} which is generated from the O-NO₂ bond scissions and/or the hydrolysis. In this way, diphenylamine which traps the NO₂ is used as a stabilizer of smokeless powder⁴⁾. And Abel test which is an evaluation method of nitric ester measures the amount of NO₂ from nitric ester.

Recently however, in our previous study, it was observed that nitrocellulose hardly released the reaction heat in the atmosphere without O₂ even if much NO₂ existed in the system⁵⁾⁻⁷⁾. In this way, we suggested that atmospheric O₂, rather than NO₂, directly contributed to heat release of nitrocellulose. There is a possibility that autoxidation, which is chain reaction by atmospheric oxygen, was conducive to spontaneous ignition. However, we investigated only nitrocellulose. Therefore, the investigation of NG which may cause the spontaneous ignition was required.

The purpose of this study is to investigate the thermal behavior of NG. In the experiments, thermal behaviors of NG under the heating condition and under the isothermal condition in various atmospheres were monitored using a heat flux calorimeter C80.

2 Experimental

2.1 Sample

2.5 mL of distilled water was added into 0.5 mL of 10 wt. % NG / ethanol provided by NOF corp. in the glass vessel. The mixture was let stand until pure NG separated. The NG was separated into the other glass vessel using a micro syringe. Small amount of water and ethanol in the NG were removed under vacuum condition.

2.2 SC-DSC

Sealed cell differential scanning calorimeter (SC-DSC, BRUKER axs), was used to measure the decomposition temperature and the amount of heat release of NG (1 ± 0.5 mg) under the heating condition (heating rate: $10 \text{ K} \cdot \text{min}^{-1}$, temperature range: 323–773 K). As the sample container, a 28 μL of Au plated cell was used.

2.3 C80

Heat flux calorimeter C80 (SETARAM) was used to observe the thermal behavior of NG (50 ± 1 mg) under the heating condition (heating rate: $0.2 \text{ K} \cdot \text{min}^{-1}$, temperature range: 323–573 K) and the isothermal condition (isothermal temperature: 393 K). As the atmospheric gases, O_2 , air, N_2 , 4 vol. % NO_2 / air, or 4 vol. % NO_2 / N_2 (Tomoe Shokai Co., Ltd.) were used. And, as the sample container, a 3.9 mL of inconel vessel (RIGAKU Co., Ltd.) was used.

3 Results and discussion

3.1 Thermal decomposition behavior of NG (SC-DSC)

When the thermal behavior of NG was investigated using SC-DSC, two exothermic peaks at 453 and 653 K were observed as shown in Fig. 1. These exothermic peaks had $3.7 \text{ kJ} \cdot \text{g}^{-1}$ and $0.9 \text{ kJ} \cdot \text{g}^{-1}$ of the amount of heat release, respectively.

The exothermic peak at 453 K would concern the decomposition of NG. In previous study, it was reported that NG has 453 K of the decomposition temperature⁸⁾. That value corresponds to the peak which was observed in this study.

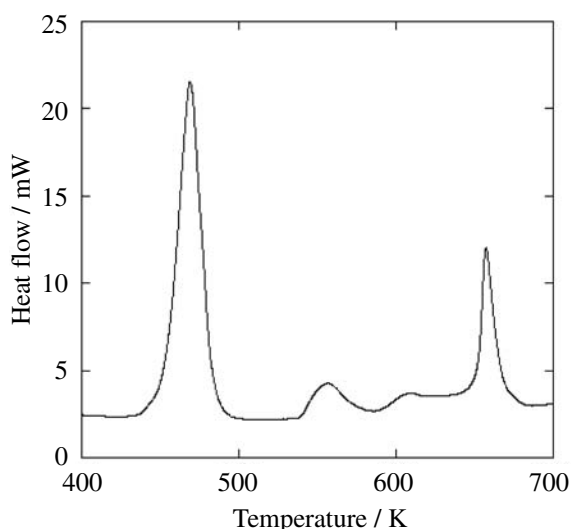


Fig. 1 Thermal behavior of NG (SC-DSC)

The exothermic peak at 653 K would be caused by the gases generated from decomposition of NG since the amount of residue of NG heated up to 573 K, the maximum test temperature of C80, was less than 5 % of NG before decomposition, and it showed no heat generation.

3.2 Effect of oxygen on the heat release of NG (C80)

When the thermal behavior of NG was observed in O_2 , air, or N_2 atmosphere, under the heating condition the thermal stability of NG was dependent on the partial pressure of O_2 as summarized in Table 1. The decomposition temperature was observed at approximately 414 K in O_2 , 426 K in air, and 428 K in N_2 . And, the amount of heat release was $3560 \text{ J} \cdot \text{g}^{-1}$ in O_2 , $3190 \text{ J} \cdot \text{g}^{-1}$ in air, and $2910 \text{ J} \cdot \text{g}^{-1}$ in N_2 , respectively. The decomposition temperature decreased and the amount of heat release increased with the partial pressure of O_2 . An increase of partial pressure of O_2 changed the behavior of heat flow against the temperature as shown in Fig. 2. In the presence of O_2 , two exothermic peaks were observed. In O_2 , first heat release was observed at 414 K and then, second one was observed at approximately 420 K. Also in air, firstly slight heat release was observed at approximately 410 K and then, larger one was observed at 426 K. On the other hand, in N_2 , only one heat release was observed at 428 K. These results indicate that the heat release at approximately 410–415 K was concerned with atmospheric O_2 . And, heat releases at approximately 420 K in O_2 , at approximately 426 K in air and at approximately 428 K in N_2 were caused by thermal decomposition of NG.

Under the isothermal condition at 393 K, the induction period was shortened in the presence of O_2 and the amount of the heat release did not depend on the presence of O_2 . Since the induction period varies even in same atmosphere, the experiments under the isothermal condition were performed three times and the intermediate values were shown in Table 2 and Fig. 3. The amount of heat release was $2380 \text{ J} \cdot \text{g}^{-1}$ in O_2 , $2680 \text{ J} \cdot \text{g}^{-1}$ in air, and $2650 \text{ J} \cdot \text{g}^{-1}$ in N_2 , respectively. Even in the absence of O_2 , NG decomposed and generated reaction heat. The induction period was observed at 4.5 h in O_2 , 4.8 h in air and 18.5 h in N_2 .

The induction period and the maximum heat release rate of NG and NC under the isothermal condition were compared. The induction period of NG and that of NC increased with the decrease of the partial pressure of O_2 as shown in Fig. 4. However, NG generated reaction heat after the induction period even in the absence of O_2 . This behavior was not observed in the case of NC.

The maximum heat release rate of NG under the isothermal condition did not change notably with the increase of the partial pressure of O_2 as shown in Fig. 5. On the contrary, the maximum heat release rate of NC increased with the increase of the partial pressure of O_2 . These results indicate that heat release behavior of NG is different from that of NC.

Table 1 Decomposition temperature and heat release of NG in various atmosphere⁹⁾.

Storage atmospheres	Decomposition temperature / K	Heat release / J·g ⁻¹
Oxygen	413	3560
Air	426	3190
Nitrogen	428	2910
4 % NO ₂ / air	387	3480
4 % NO ₂ / N ₂	428	3130

Table 2 Induction period and heat release of NG in various atmosphere⁹⁾.

Storage atmospheres	Induction period / h	Heat release / J·g ⁻¹
Oxygen	4.5	2380
Air	4.8	2680
Nitrogen	18.5	2650
4 % NO ₂ / air	—	—
4 % NO ₂ / N ₂	9.7	2950

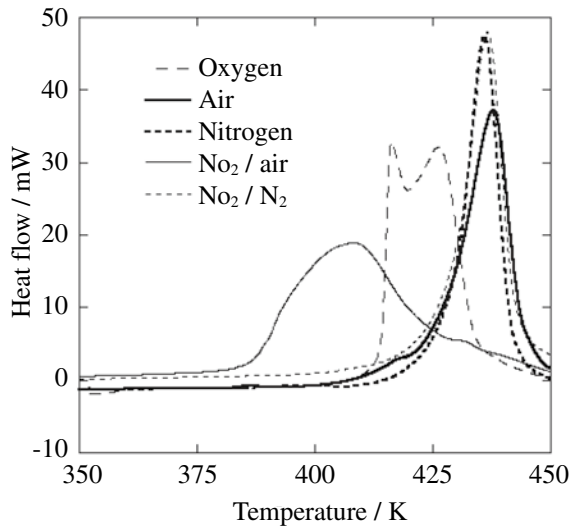


Fig. 2 Thermal behavior of NG under the heating condition (C80).

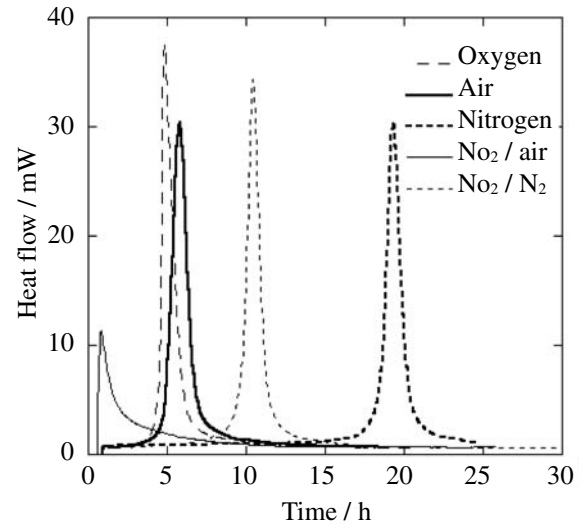


Fig. 3 Thermal behavior of NG under the isothermal condition (C80).

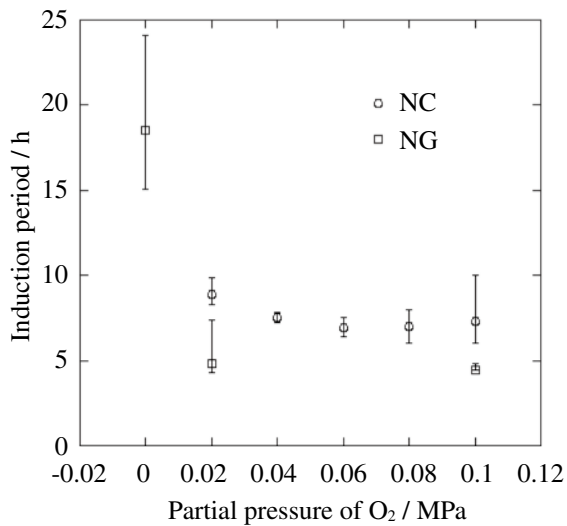


Fig. 4 Induction period vs. partial pressure of O₂.

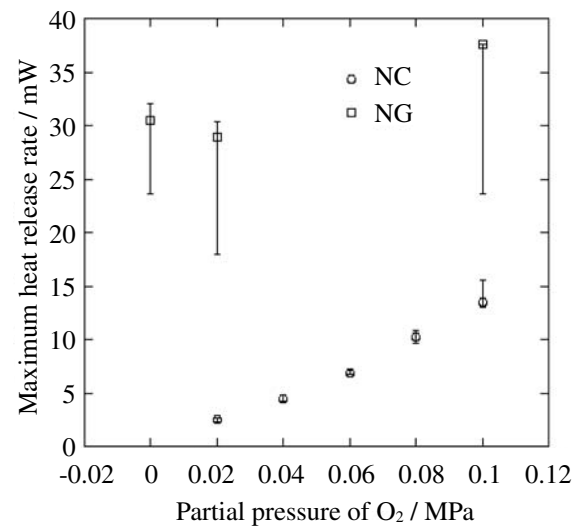


Fig. 5 Maximum heat release rate vs. partial pressure of O₂.

3.3 Effect of nitrogen dioxide on the heat release of NG (C80)

NO₂ contributed to decomposition of NG in the presence of O₂ under the heating condition. When thermal behavior of NG was observed in 4 vol. % NO₂ / N₂ or 4 vol. % NO₂ / air, the decomposition temperature and the amount of heat release are summarized in Table 1 and the heat flow against the temperature is shown in Fig. 2. The heat release in 4 vol. % NO₂ / N₂ was observed at 428 K with

3130 J·g⁻¹, and no heat release was observed at approximately 410-415 K. Contrary, the decomposition temperature in 4 vol. % NO₂ / air was observed at 387 K. The decomposition temperature was extremely lower than that in 4 vol. % NO₂ / N₂.

Under the isothermal condition at 393 K, the induction period was shortened in the presence of NO₂ as shown in Fig. 3. In 4 vol. % NO₂ / air, the induction period was so short that the induction period was not able to calculated

because NG decomposed under 393 K. That result indicates that NO₂ contributed to decomposition of NG notably in the presence of O₂. In 4 vol. % NO₂ / N₂ the induction period was observed at 9.7 h. This result indicates that NO₂ would contribute to decomposition of NG even in the absence of O₂ while NC did not release reaction heat in NO₂ / N₂.

4. Conclusions

In order to investigate the heat release behaviors of NG, the thermal analysis of NG was performed. Following conclusions can be made.

- I. O₂ contributed to decomposition of NG.
- II. NO₂ in the presence of O₂ contributed to decomposition of NG more than NO₂ in the absence of O₂.

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ニトログリセリンの熱的挙動に関する研究

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ニトログリセリン (NG) の自然発火挙動を把握するために様々な雰囲気中、昇温および等温条件で熱分析を行った。昇温測定ではO₂存在下で416 K, 436 K付近でそれぞれ発熱ピークが得られ、低温側ピークの発熱量はO₂分圧に依存した。一方、N₂雰囲気では416 K付近に発熱ピークは観察されなかった。NO₂ / N₂雰囲気でもその温度付近では発熱ピークは観察されなかったが、NO₂ / 空気雰囲気では387 K付近に大きな発熱ピークが観測された。等温測定ではO₂が存在する雰囲気では誘導期が短くなった。また、NO₂ / 空気雰囲気の誘導期は空気雰囲気より短くなり、NO₂ / N₂雰囲気の誘導期はN₂雰囲気の誘導期より短くなった。このことよりNO₂はNGの分解を促進するが、O₂と共存するとNO₂単独よりもより分解を促進することがわかった。

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