

Study on the spontaneous ignition mechanism of nitric esters (III)

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Received 12 October 2004; received in revised form 7 December 2004; accepted 5 February 2005

Abstract

The spontaneous ignition mechanism of three types of smokeless powders such as cellulose nitrate/potassium sulfate (SB), cellulose nitrate/glycerin trinitrate/potassium sulfate (DB), and cellulose nitrate/glycerin trinitrate/nitroguanidine/potassium sulfate (TB) were analyzed in terms of the thermal behavior and the pressure change during the isothermal storage at 393 K in various gases. The heat release of SB and DB was suppressed in the atmosphere without O₂ and even in 4.5 vol.% NO₂/N₂. However, in 4.7 vol.% NO₂/air, the exothermic reaction was accelerated compared to that in dry air. In addition, the total pressure decreased during the storage in the presence of O₂. This nature of the behavior of SB and DB indicated that autoxidation, which was propagation with O₂ and radical species derived from NC, was involved in the exothermic reaction. And, NO₂ contributed not to the autoxidation but to the initiation process before the autoxidation occurred. On the other hand, the exothermic reaction of TB might be different from that of SB and DB because TB released the reaction heat in no O₂ atmosphere such as 4.5 vol.% NO₂/N₂. TB would react with NO₂ without O₂ and release the reaction heat when NO₂ was excessively present in the system. This specific nature would be due to the presence of 50 wt.% of nitroguanidine which was not nitric ester.

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Keywords: Cellulose nitrate; Nitric ester; Smokeless powder; Autoxidation

1. Introduction

Nitric esters are widely used as an ingredient in propellants and dynamites in spite of its unstable character, which is liable to undergo spontaneous ignition. The spontaneous ignition of nitric esters has caused serious accidents, and such tragedies have been reported even in recent years.

In particular, the spontaneous ignition mechanism of cellulose nitrate (NC) has been investigated for a long time. Some reviews [1,2] suggested that the spontaneous ignition was caused by the reaction between NC and NO₂. The NO₂ originated from the O–NO₂ bond scissions or the hydrolysis. This mechanism has been widely accepted as the ignition mechanism. Based on the mechanism, the Japanese Industrial Standards stipulates the stability test.

Recently, we have reported that the exothermic reaction of NC hardly took place without O₂ even if NO₂ was excessively present in the system [3–6]. NO₂ accelerated the heat release in the presence of O₂. The nature of the exothermic reaction is thought to be autoxidation caused by atmospheric O₂. However, the mechanism of the spontaneous ignition was analyzed only for NC and whether the mechanism can be applied to actual propellants, which contain not only NC but other substances as well, was still unknown. Therefore, the investigation of analyzing spontaneous ignition mechanism for actual propellants was attempted here.

Nitric ester-based propellants are called smokeless powders. Three types of smokeless powder can be classified by their composition: single base powder (SB) consists of NC, double base powder (DB) consists of NC and nitroglycerine, and triple base powder (TB) is composed of NC, nitroglycerine and nitroguanidine. Each smokeless powder also contains small amount of additives such as stabilizers and flash reduc-

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ing agents. Those additives are used differently depending on the application.

In this paper, the spontaneous ignition mechanism of SB, DB, and TB were analyzed in terms of the thermal behavior and the pressure change during isothermal storage in various gases.

2. Experimental

2.1. Sample

The SB, DB, and TB without any stabilizer were supplied by NOF Corp. Their compositions were shown in Table 1. Nitrogen contents of the cellulose nitrate was 12.27 wt.%. Potassium sulfate was added into NC as flash reducing agent.

2.2. Measurement

The sample (50 mg) was placed in approximately 3.7 cm³ vessels (Rigaku Corp.). The air in the vessel was replaced by O₂, dry air, N₂, 4.7 vol.% NO₂/air, and 4.5 vol.% NO₂/N₂ (Suzuki Shokan Corp., Ltd.), respectively. This procedure was repeated 4–5 times to ensure complete replacement. The sample was stored using C-80 (SETARAM S.A.) at 393 K to observe the thermal behavior and the whole pressure change during isothermal storage.

3. Results and discussion

3.1. SB

In O₂, the thermal behavior of SB indicated the reaction heat of 3170 mJ g⁻¹ with a approximately 20 h induction period (Fig. 1). The induction period was obtained from the intersection of a tangent on the maximum inclination point of heat flow and the line of heat flow = 0. In N₂, dry air, or 4.5 vol.% NO₂/N₂, no heat release was observed at least 80 h.

NO₂ accelerated the exothermic reaction of SB in the presence of O₂. The reaction heat was observed in 4.7 vol.% NO₂/air whereas the reaction heat was not observed in 4.5 vol.% NO₂/N₂.

SB seemed to release the reaction heat less active than NC did [3–6] maybe due to its rougher particle size than NC in the experiments.

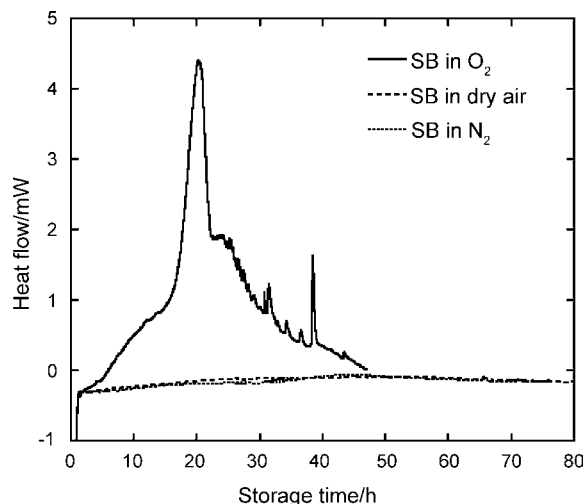


Fig. 1. Thermal behavior of SB in O₂, dry air, and N₂, storage temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of SB: 50 mg.

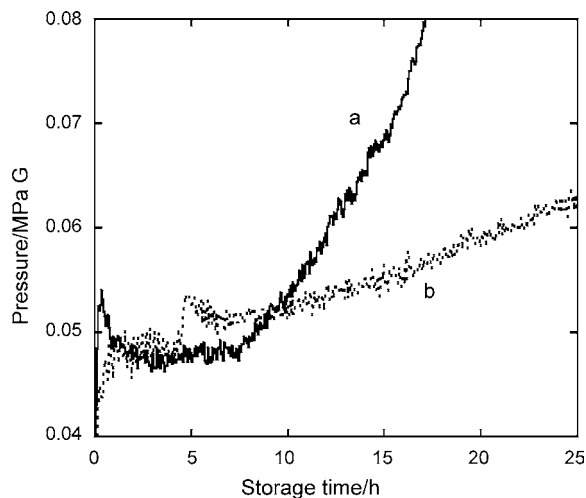
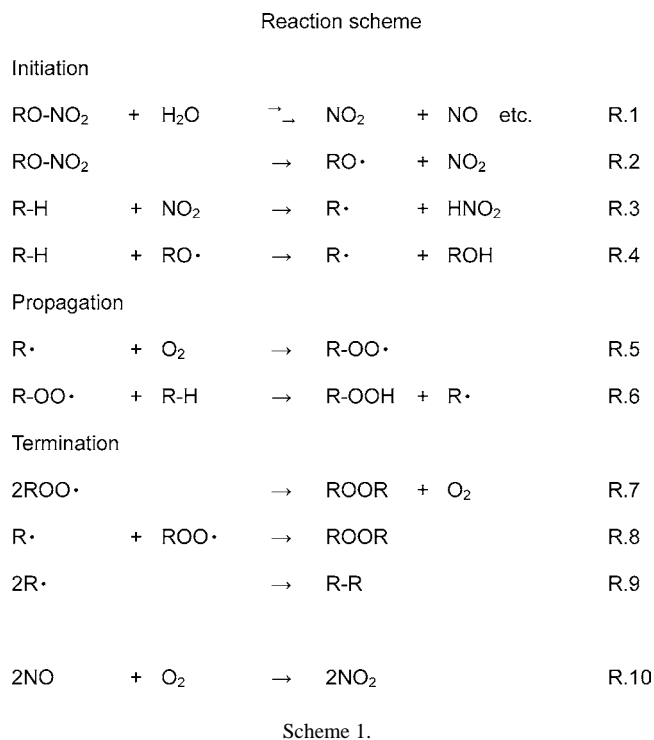


Fig. 2. Pressure change of SB during storage (a) storage in O₂; (b) storage in N₂, storage temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of SB: 50 mg.

In the case of that SB was stored in O₂, the pressure gradually decreased (Fig. 2). The pressure decrease of approximately 5×10^{-3} MPa was observed until the duration reached 8 h, and then the pressure gently rose. In N₂, the pressure did not decrease; the pressure linearly increased. In previous study [11], similar pressure decrease was ob-

Table 1
Composition of the samples

	Composition (wt.%)			
	Cellulose nitrate	Nitroglycerine	Nitroguanidine	Potassium sulfate
Single base	99	–	–	1
Double base	59	40	–	1
Triple base	29	20	50	1



served during storage of NC in the presence of O₂. And, it was confirmed the pressure decrease was due to the decrease of O₂. Therefore, the pressure decrease of SB would be due to the decrease of the partial pressure of O₂.

The nature of SB would indicate that O₂ mainly contributed to the exothermic reaction, and NO₂ played the important role in the reaction, which hardly participated in the exothermic reaction. In the Scheme 1 of the spontaneous ignition for NC, we have proposed [3–6] NO₂ was generated in the initiation process (R.s 1–4) [7,8]. The initiation process was followed by the autoxidation which was proceeded with R· and ROO· (R.s 5,6) [9,10]. In the termination process, those radicals were deactivated (R.s 7–9). The latter two processes are quite conducive to heat release since each reaction in those processes releases more reaction heat than that in initiation process. Since the thermal behavior of SB was quite similar to that of NC, it might be explained by this mechanism too.

3.2. DB

The exothermal behavior of DB during the isothermal storage at 393 K was not observed without presence of O₂ (Fig. 3). The amounts of reaction heat of DB in O₂ and in dry air were 1580 and 1390 mJ g⁻¹, and it seemed to depend on the partial pressure of O₂. These results indicated that oxygen, rather than NO₂, directly contributed to the exothermic reaction.

The induction periods of exothermic reaction for DB during the isothermal storage at 393 K in 4.7 vol.% NO₂/dry air and in dry air were 3 and 7 h, respectively (Fig. 4). In addition, each amount of reaction heat in 4.7 vol.% NO₂/air and in dry air was in agreement (in dry air: 1390 mJ g⁻¹; in

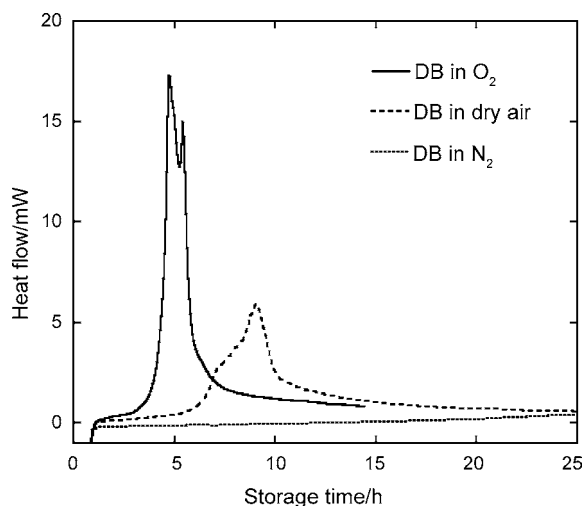


Fig. 3. Thermal behavior of DB in O₂, dry air, and N₂, storage temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of DB: 50 mg.

4.7 vol.% NO₂/air: 1310 mJ g⁻¹). These results indicated that NO₂ played the important role not in the exothermic reaction but in the initiation reaction (Fig. 5).

The thermal behavior of DB as well as that of SB could be explained by the mechanism as shown in the Scheme 1.

The induction period was shortened in company with increase in the initial pressure of O₂. The thermal behavior in O₂ indicated the reaction heat with a approximately 4 h induction period, and that in dry air did with a approximately 7 h induction period. That showed the initiation process was accelerated with increase of O₂ concentration.

Volltrauer and Fontijn [12] and Nakamura and co-workers [13] suggested NO was the major component in gases evolved from NC. Therefore, the reaction described in the R.10 (reaction of NO with O₂) might play an important role in terms of the NO₂ generation.

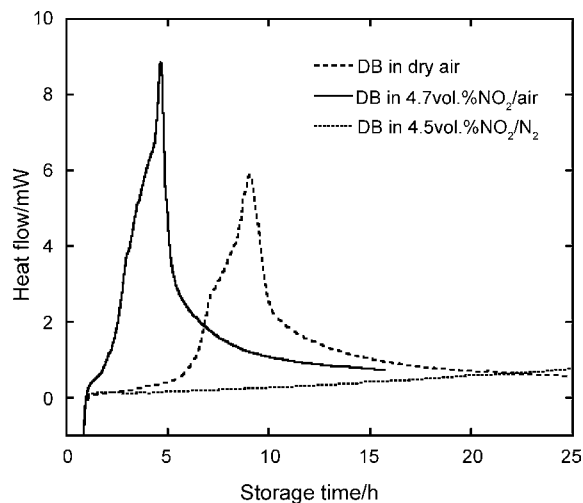


Fig. 4. Thermal behavior of DB in dry air, 4.7 vol.% NO₂/air, and 4.5 vol.% NO₂/N₂, storage temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of DB: 50 mg.

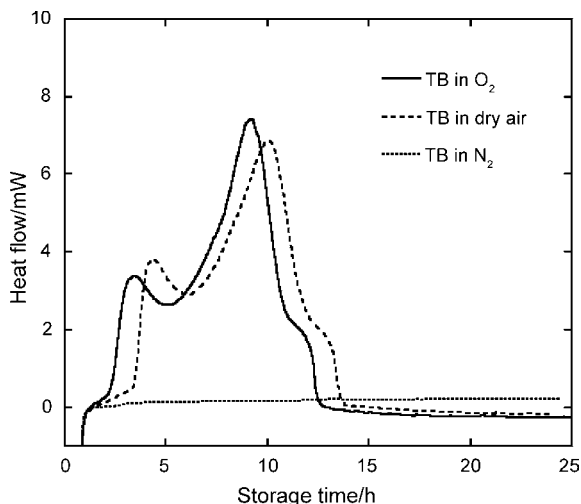


Fig. 5. Thermal behavior of TB in O_2 , dry air, and N_2 , storage temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of TB: 50 mg.

The thermal behavior of DB might not be affected by particle size at 393 K since DB melted at less than that temperature.

3.3. TB

The exothermal behavior of TB during the isothermal storage at 393 K was different from that of SB and DB. The heat release was observed not in N_2 , but in O_2 , in dry air, and in 4.5 vol.% NO_2/N_2 and the amounts were 2770, 2790, and 2700 $mJ g^{-1}$ of, respectively (Fig. 6). This showed TB released the reaction heat only by NO_2 . Therefore, the reac-

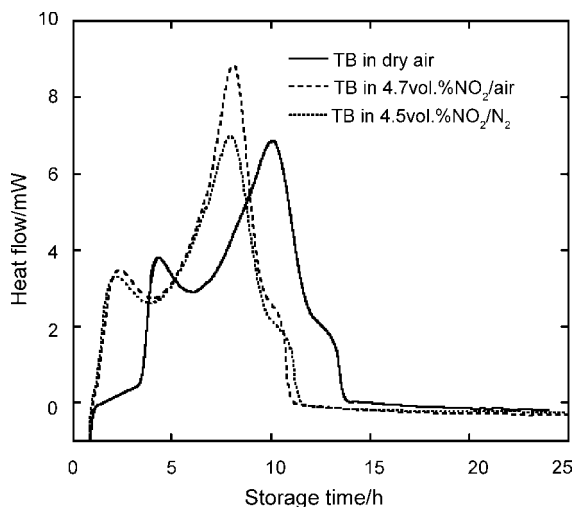


Fig. 6. Thermal behavior of TB in dry air, 4.7 vol.% NO_2 /air, and 4.5 vol.% NO_2/N_2 , storage temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of TB: 50 mg.

tion mechanism of TB seemed to be different from that of SB and DB. This specific nature would be due to the presence of 50 wt.% of nitroguanidine which was not nitric ester.

4. Conclusion

The spontaneous ignition mechanism of three types of smokeless powders such as SB, DB, and TB was analyzed in terms of the thermal behavior and the pressure change during isothermal storage in various gases.

The heat release of SB and DB was suppressed in the atmosphere without O_2 . Even in 4.5 vol.% NO_2/N_2 , the reaction heat was hardly observed. In 4.7 vol.% NO_2 /air, the exothermic reaction was accelerated in comparison with that in dry air. In addition, the total pressure decreased during storage in dry air and O_2 . This nature of the behavior of SB and DB indicated that autoxidation was involved in the exothermic reaction. And, NO_2 contributed not to the autoxidation but to the initiation process before the autoxidation.

TB released the reaction heat even in 4.5 vol.% NO_2/N_2 . TB might release the reaction heat only by NO_2 when NO_2 was excessively present in the system. The exothermic reaction of TB might be different from that of SB and DB.

Acknowledgment

This work was partly supported by financial aid for research promotion from the Japan Explosives Society. We greatly acknowledge their support.

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