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

Katsumi Katoh[a, *], Lu Le[a], Mieko Kumasaki[b], Yuji Wada[c], Mitsuru Arai[a]

[a] Graduate School of Frontier Sciences, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[b] National Institute of Industrial Safety, 1-4-6 Umezono, Kiyose-shi, Tokyo 204-0024, Japan
[c] National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba-shi, Ibaraki 305-8565, Japan

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Abstract

The thermal behavior of cellulose nitrate (NC) with diphenyl amine (DPA) or a phenol-based oxidation inhibitor (AO80) was investigated in order to estimate the effect as a stabilizer in a smokeless powder. During the isothermal storage at 393 K, both stabilizers decreased the amount of the reaction heat of NC, and lengthened the induction period of the exothermic reaction. Those effects might indicate that both stabilizers were capable of suppressing the spontaneous ignition. However, the effects of DPA and AO80 on the isothermal storage of NC were different. Under the storage in O_2, DPA showed larger effect on the induction period but less effect on the released heat reduction than AO80 did. Those differences might be understood as follows: DPA mainly prevented the reaction before the autoxidation by trapping NO_2, while AO80 mainly prevented the autoxidation of NC by trapping $ROO^\bullet$.

Keywords: Cellulose nitrate; Autoxidation; Diphenyl amine; Oxidation inhibitor

1. Introduction

Cellulose nitrate (NC) is widely used as an ingredient of propellants and dynamites in spite of its unstable characteristic such as spontaneous ignition. The spontaneous ignition of NC has caused serious accidents, which have been reported even in recent years.

The spontaneous ignition mechanism of 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 NO_2. The NO_2 originated from the $O–NO_2$ bond scissions or the hydrolysis. In order to stabilize NC, the stabilizer such as diphenyl amine (DPA) is added. As for DPA stabilization mechanism, it is known that DPA traps NO_2 and terminates the exothermic reaction. However, the stabilization mechanism is not fully understood yet. Therefore, the investigation of the NC stabilization mechanism by DPA is required.

Recently, we reported that an exothermic reaction of NC hardly took place without O_2 [3–6] during the isothermal storage of NC, and O_2, rather than NO_2, directly contributed to the exothermic reaction. The nature of the exothermic reaction was thought to be autoxidation caused by atmospheric O_2. Accordingly, a phenol-based oxidation inhibitor (AO80), which interferes with the autoxidation, is expected to stabilize NC. AO80 is anticipated to be a new stabilizer for preventing the spontaneous ignition of NC based on our proposed reaction scheme.

The object of this study is to estimate the effect of DPA and AO80 on the NC stability. In the experiments, the thermal behavior was monitored using C-80 during isothermal storage.

2. Experimental

2.1. Sample

NC in 2-propanol (nitrogen content, 12 wt.%; Sigma–Aldrich Corp.) was dried in vacuo at approximately 298 K

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* Corresponding author. Tel.: +81 3 5841 7293; fax: +81 3 5841 7225.
E-mail address: k_katoh@explosion.t.u-tokyo.ac.jp (K. Katoh).

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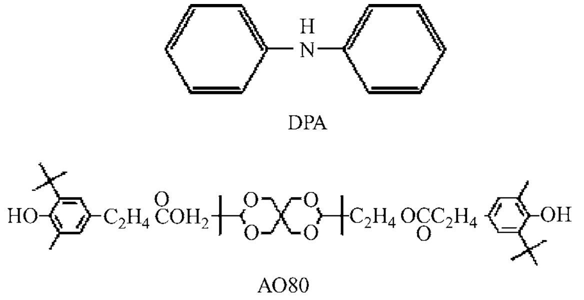

Fig. 1. Chemical structure of DPA and AO80.

for 3–4 days. Particles with a diameter of less than 100 μm were prepared by sieving, and then the NC was again dried under the same conditions for 1–2 days. After drying, DPA or AO80 was added to the NC (50 mg). The chemical structures of DPA and AO80 are shown in Fig. 1. The NC with DPA or AO80 was placed in vessels (3.7 cm^3). The air in the vessel was removed in vacuo and then replaced by dry air or O_2 (Suzuki Shokan Corp., Ltd.). This procedure was repeated 4–5 times to ensure complete replacement.

2.2. Measurement

The sample was stored in C-80 (SETARAM S.A.) at 393 K to observe the thermal behavior during isothermal storage.

3. Results

3.1. Effect of DPA on stabilization

The isothermal storage of NC with and without DPA at 393 K indicated that DPA affected the heat release reaction of NC. In dry air, 1 wt.% DPA/NC released 160 J g^{-1} of the reaction heat with a 20 h induction period while NC without DPA released 520 J g^{-1} of the reaction heat with an 8 h induction period (Fig. 2). 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. Two weight percentage of DPA/NC showed no heat release even after a 48 h storage.

The O_2 atmosphere accelerated the heat release and NC without DPA released 2390 J g^{-1} of the reaction heat in 7 h. However, DPA reduced the heat release of NC even in O_2. An amount of 1 and 2 wt.% of DPA/NC did not release the reaction heat until the storage period reached 20 and 35 h, and also reduced the amount of the reaction heat from 2390 to 2320 and 2160 J g^{-1}, respectively (Fig. 3).

3.2. Effect of AO80 on stabilization

It was newly discovered that AO80 also might have a stabilization ability for NC. In isothermal storage in dry air at 393 K, the induction period of AO80/NC was observed after storage for 11, 13, and 14 h with 1, 2, and 4 wt.% contents, respectively, while NC without AO80 was observed with 8 h induction period (Fig. 4). And the amount of reaction heat of AO80/NC decreased from 520 to 330, 260, and 150 J g^{-1} with 1, 2, and 3 wt.% contents.

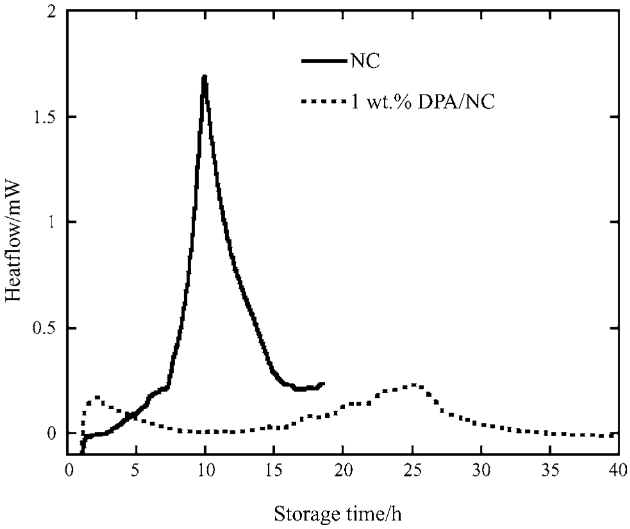

Fig. 2. Thermal behavior of DPA/NC in dry air. Storage temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of NC: 50 mg.

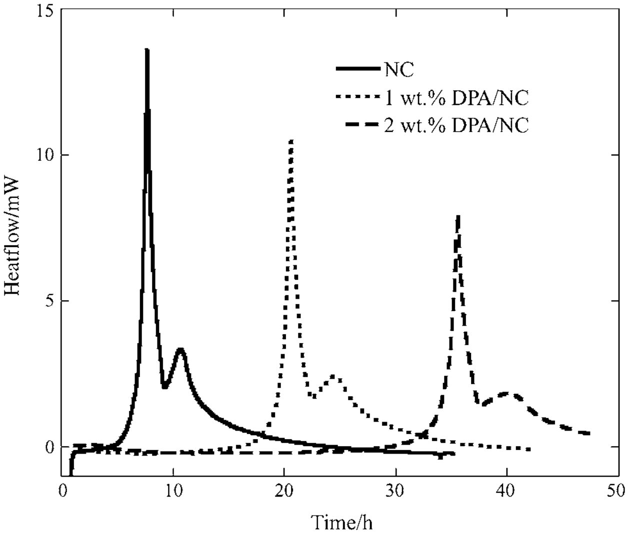

Fig. 3. Thermal behavior of DPA/NC in O_2. Storage temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of NC: 50 mg.

In O_2, 1, 2, and 3 wt.% AO80 lengthened the induction period from 7 to 10, 12, and 15 h, and those decreased the amount of reaction heat from 2390 to 2130, 1950, and 1800 J g^{-1}, respectively (Fig. 5).

4. Discussion

In the previous study [3–6], we proposed the spontaneous ignition mechanism of NC as shown in the reaction Scheme 1. The reactions, R.1–4, describe the initiation process during

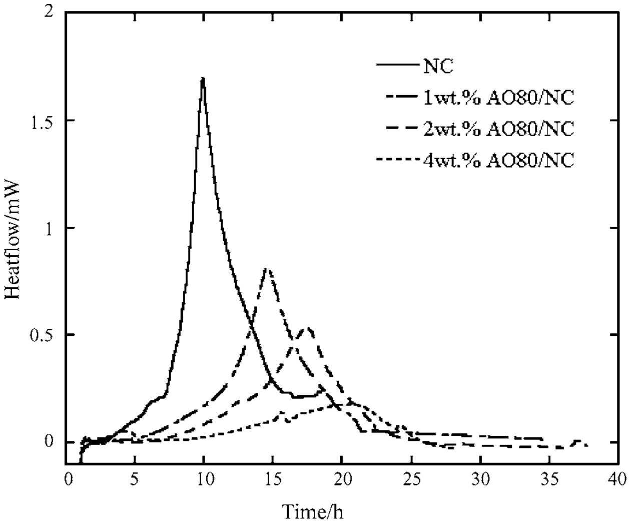

Fig. 4. Thermal behavior of AO80/NC in dried air. Storage temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of NC: 50 mg; exothermic upwards.

Initiation

$RO\text{-}NO_2 + H_2O \rightarrow NO_2 + NO$ etc. R.1

$RO\text{-}NO_2 \rightarrow RO\bullet + NO_2$ R.2

$R\text{-}H + NO_2 \rightarrow R\bullet + HNO_2$ R.3

$R\text{-}H + RO\bullet \rightarrow R\bullet + ROH$ R.4

Propagation

$R\bullet + O_2 \rightarrow R\text{-}OO\bullet$ R.5

$R\text{-}OO\bullet + R\text{-}H \rightarrow R\text{-}OOH + R\bullet$ R.6

Termination

$2ROO\bullet \rightarrow ROOR + O_2$ R.7

$R\bullet + ROO\bullet \rightarrow ROOR$ R.8

$2R\bullet \rightarrow R\text{-}R$ R.9

Scheme 1.

the degradation of NC. They show that the bond scission and the hydrolysis of O–NO_2 bond occur (R.1 and 2), and then NO_2 and $RO^\bullet$ abstract the hydrogens from NC (R.3 and 4). The overall initiation process generates $R^\bullet$ [7,8]. The generation of $R^\bullet$ starts the propagation called autoxidation (R.5 and 6) [9,10]. During the propagation process, O_2 molecule in the ambient gas reacts with $R^\bullet$, and produced $ROO^\bullet$ abstracts hydrogen NC. In this reaction scheme, it is considered that the propagation process and the subsequent termination process are quite conducive to heat release since each reaction in those processes releases more reaction heat than that in initiation process.

The thermal behaviors of DPA/NC and AO80/NC were different from another in the induction period and the amount of reaction heat. In O_2, the induction period of DPA/NC was extended significantly (Fig. 6), while the reduction of the reaction heat of DPA/NC was less than that of AO80/NC (Fig. 7). It is known that DPA traps NO_2 [11]. From this, it can be said that DPA trapped NO_2 and, thus, DPA mainly takes effect on the initiation process which hardly contributed to the heat release.

For AO80/NC under O_2, the induction period increased slightly, and the reaction heat decreased significantly. This phenomenon might be due to the radical trapping character of AO80 to suppress autoxidation. AO80 is well known for deactivating $ROO^\bullet$ as shown in Fig. 8 [12]. Therefore, it was considered that AO80 trapped $ROO^\bullet$ generated in the autoxidation (R.4) and, thus, AO80 prevented the propagation which was conductive to the heat release.

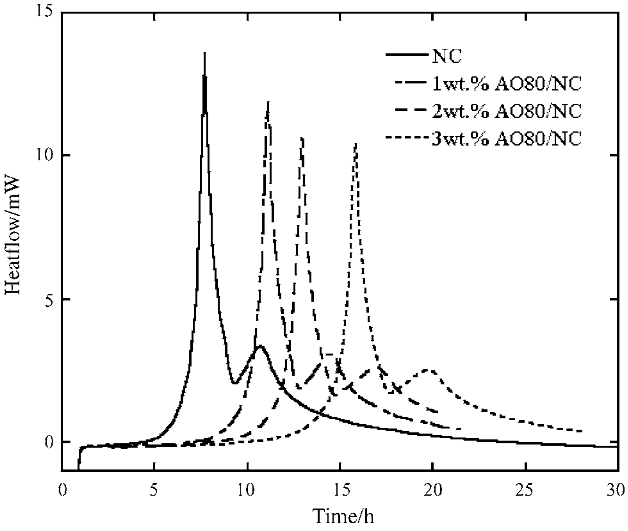

Fig. 5. Thermal behavior of AO80/NC in O_2. Storage temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of NC: 50 mg; exothermic upwards.

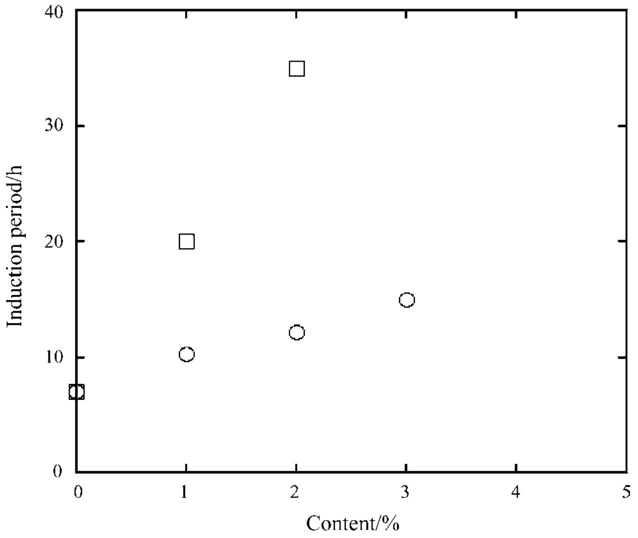

Fig. 6. Relationship between induction period and content of stabilizer in O_2. □: DPA, ○: AO80, temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of NC: 50 mg.

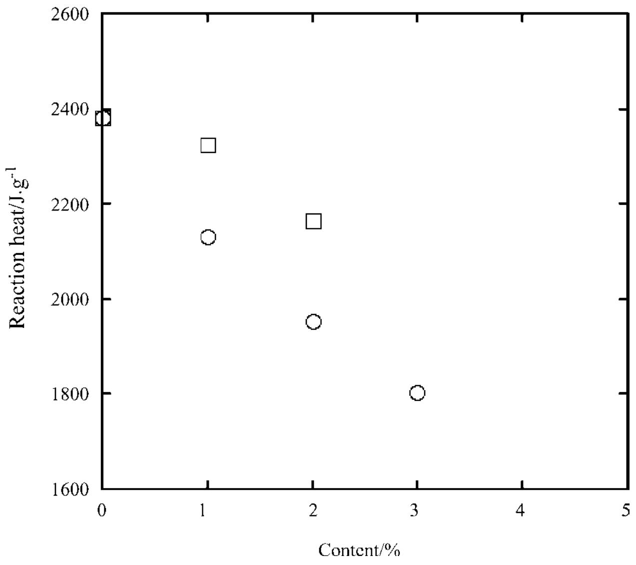

Fig. 7. Relationship between amount of reaction heat and content of stabilizer in O_2. □: DPA, ○: AO80, temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of NC: 50 mg.

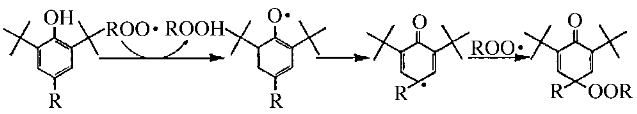

Fig. 8. Stabilization mechanism of AO80.

The behavior in dry air was different from that in O_2 (Figs. 9 and 10). The reaction heat of DPA/NC decreased more than that of NC/AO80. Those differences might be understood as follows: in limited O_2 atmosphere such as the dry air, $R^\bullet$ which was reduced by DPA was quenched before the reaction proceeded to autoxidation.

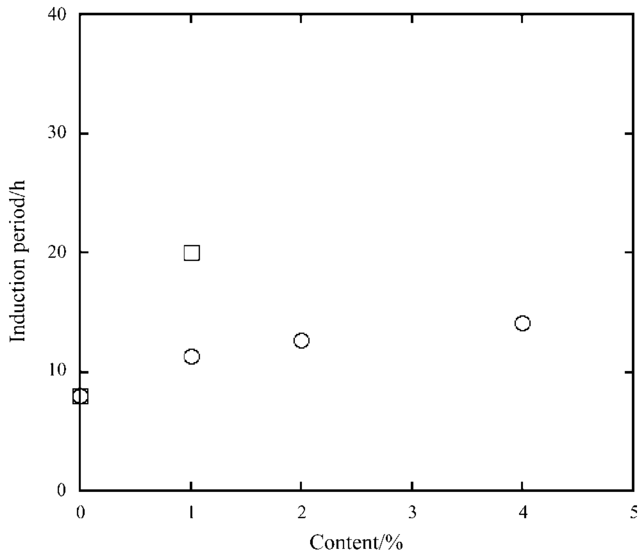

Fig. 9. Relationship between induction period and content of stabilizer in dry air. □: DPA, ○: AO80, temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of NC: 50 mg.

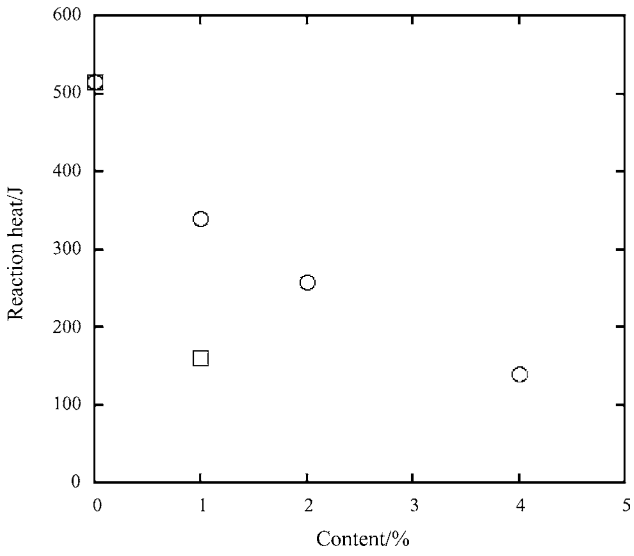

Fig. 10. Relationship between amount of reaction heat and content of stabilizer in dry air. □: DPA, ○: AO80, temperature: 393 K, initial pressure: 0.1 MPa at room temperature, initial amount of NC: 50 mg.

5. Conclusion

The thermal behavior of NC with DPA or AO80 was investigated in order to estimate the effect as a stabilizer in a smokeless powder.

During isothermal storage at 393 K, both stabilizers decreased the amount of the reaction heat of NC, and lengthened the induction period of the exothermic reaction. Those effects might indicate that both stabilizers were capable of suppressing the spontaneous ignition.

However, the effects of DPA and AO80 on the isothermal storage of NC were different. DPA showed larger effect on the induction period but less effect on the released heat reduction than AO80 did. Those differences might be understood as follows: DPA mainly prevented the reaction before the autoxidation by trapping NO_2, while AO80 mainly prevented the autoxidation of NC by trapping $ROO^\bullet$.

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