

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

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Abstract

The spontaneous ignition mechanism of cellulose nitrate (NC) was analyzed in terms of the pressure change and the thermal behavior during isothermal storage at 393 K. During storage of the NC, atmospheric O₂ was consumed during an exothermic reaction. The heat release behavior as well as the O₂ decreasing behavior could be fitted to a first-order reaction. The rate constant (K) and the induction period (t_{indc}) for the heat release behavior almost coincided with those for the O₂ decreasing behavior (O₂ decreasing behavior: $K = 7.7 \times 10^{-5} \text{ s}^{-1}$, $t_{\text{indc}} = 10 \text{ h}$; heat release behavior: $K = 8.1 \times 10^{-5} \text{ s}^{-1}$, $t_{\text{indc}} = 9.2 \text{ h}$). The reaction heat did not increase even if the initial amount of NC increased under a limited O₂ condition. These results would suggest that NC released reaction heat due to autoxidation which was propagation involving O₂ and radical species generated from NC. Even in a 4.7 vol.% NO₂/air atmosphere, the amount of reaction heat did not significantly change from those in dry air. The reaction order was also not affected by the partial pressure of NO₂. On the one hand, the K was slightly higher, and the t_{indc} was shorter in the 4.7 vol.% NO₂/air ($K = 1.8 \times 10^{-4} \text{ s}^{-1}$; $t_{\text{indc}} = 3.4 \text{ h}$) than those in dry air. These results would indicate that NC accumulated reaction heat due to autoxidation by atmospheric O₂, and NO₂ contributed to the initiation process before the autoxidation occurred.

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1. Introduction

Cellulose nitrate (NC) is 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 NC has caused serious accidents, and such tragedies have been reported even in recent years.

The spontaneous ignition mechanism of NC has been investigated for a long time. Some reviews [1,2] described the cause of the spontaneous ignition as heat accumulation. The heat was generated during the reaction between NC and NO₂. NO₂ was considered to originate by the O–NO₂ bond scission or the hydrolysis. This mechanism has been widely accepted

as the ignition mechanism, and Japanese Industrial Standards stipulates a stability test for NC based on it.

Contrary to the ignition mechanism including NO₂, Kimura and coworker [3–5] suggested that atmospheric O₂ contributed to the spontaneous ignition using a chemical luminescence analysis technique. In addition, they recently suggested that unstable substances such as peroxides were produced during a long-term storage [5,6].

A likely explanation for the controversial mechanism may be that not only NO₂, but also O₂ participates in the spontaneous ignition, and then peroxides are generated in the reaction between these gases and NC. In the previous study [7–10], we have reported that an exothermic reaction hardly took place without O₂ even if NO₂ was excessively present in the storage atmosphere. The reaction with O₂, rather than the reaction with NO₂, directly contributed to the exothermic reaction. This might indicate that the exothermic reaction

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mechanism was due to autoxidation caused by atmospheric O₂. Therefore, the spontaneous ignition mechanism needs to be clarified for safe storage.

In this paper, the spontaneous ignition mechanism was analyzed in terms of the pressure change and the thermal behavior during isothermal storage.

2. Experimental

2.1. Sample

NC in 2-propanol (N contents: 12 wt.%; Sigma–Aldrich Corp.) was dried in vacuo at ambient temperature for 3–4 days. Particles with a diameter of less than 100 μm were prepared with a sieve, and then the NC was again dried under the same conditions for 1–2 days. The dried NC (50 mg) was placed in the vessel (Rigaku Corp.) having a capacity of approximately 3.7 cm³ (Fig. 1). The air in the vessel was removed in vacuo and then replaced by dry air, 4.7 vol.% NO₂/air, or an O₂/N₂ mixture gas with different O₂ partial pressure (Suzuki Shokan Corp. Ltd.). This procedure was repeated four to five times to ensure complete replacement of the ambient gases.

2.2. Measurement

The NC was stored using C-80 (SETARAM S.A.) at 393 K to observe the overall pressure change and the thermal behavior during the isothermal storage.

In addition, the NC was stored in a constant temperature bath (Yamato Corp.) at 393 K. After storage, the ambient gas in the vessel was analyzed by gas chromatography (Shimadzu Corp. GC8A, TCD). The O₂ partial pressure was determined in comparison with the N₂ partial pressure based on the assumption that the absolute amount of N₂ did not change.

3. Results and discussion

3.1. Chemical kinetics

In the previous study [7–10], we proposed the spontaneous ignition mechanism of NC as shown by Scheme 1.

Eqs. (R1)–(R4), describe the initiation process during the degradation of NC. They show that the bond scission and the hydrolysis of O–NO₂ bond occur (Eqs. (R1) and (R2)), and then NO₂ and RO• abstract the hydrogen from NC (Eqs. (R3) and (R4)). The overall initiation process generates R• [11,12].

The generation of R• starts the propagation called autoxidation [13,14] (Eqs. (R5) and (R6)). During the propagation process, an O₂ molecule in the ambient gas reacts with R•, and a produced ROO• abstracts a hydrogen. In Scheme 1, it is considered that the propagation and the subsequent termi-

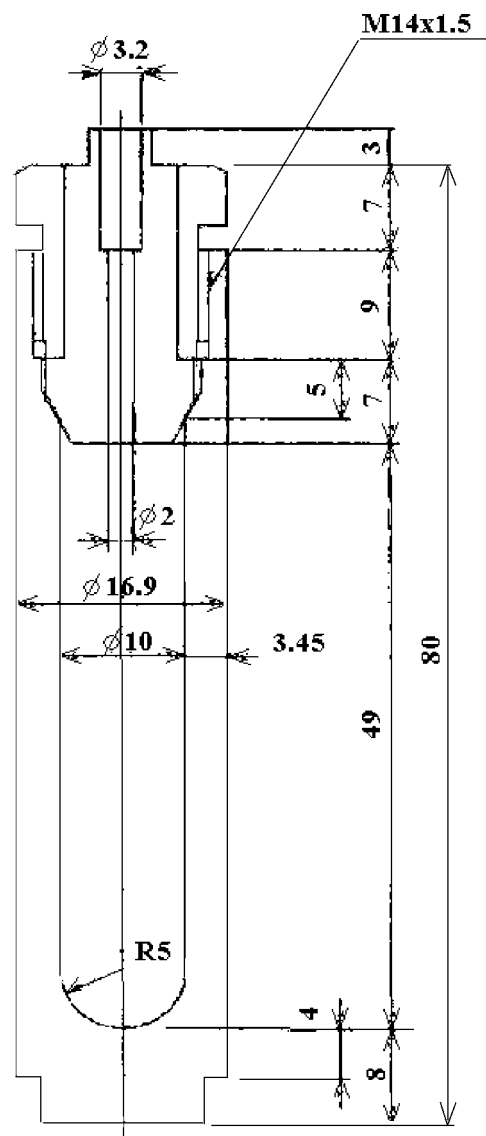


Fig. 1. The draft for the calorimeter vessel (mm).

nation process are quite conducive to heat release since each reaction in those processes releases more reaction heat than that in the initiation process.

For the autoxidation mechanism, the rate equation of O₂ decrease can be written as follows:

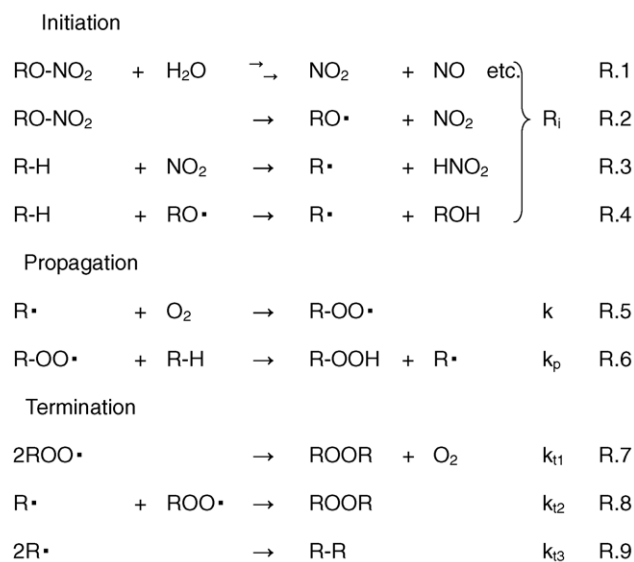
$$-\frac{d[\text{O}_2]}{dt} = k[\text{O}_2][\text{R}^\bullet] \quad (1)$$

Given that a steady-state approximation is applied for the O₂ decrease rate equation (Eq. (1)), the rate of initiation, R_i , is same as the rate of the termination process. Accordingly, R_i is

$$R_i = k_{t1}[\text{ROO}^\bullet]^2 + k_{t2}[\text{R}^\bullet][\text{ROO}^\bullet] + k_{t3}[\text{R}^\bullet]^2 \quad (2)$$

For $k_{t2} = 2(k_{t1}k_{t3})^{1/2}$, Eq. (2) is transcribed into Eq. (3):

$$R_i = (k_{t1}^{1/2}[\text{ROO}^\bullet] + k_{t3}^{1/2}[\text{R}^\bullet])^2 \quad (3)$$



Scheme 1.

When only R• is generated during the initiation process and the steady-state approximation applies to R•:

$$R_i + k_p[\text{ROO}\bullet][\text{RH}] = k[\text{R}\bullet][\text{O}_2] + k_{t_3}^{1/2}[\text{R}\bullet]R_i^{1/2} \quad (4)$$

is obtained. Similarly, when the steady-state approximation applies to ROO•:

$$k[\text{O}_2][\text{R}\bullet] = k_p[\text{RH}][\text{ROO}\bullet] + k_{t_1}^{1/2}[\text{ROO}\bullet]R_i^{1/2} \quad (5)$$

is obtained. From Eqs. (4) and (5), [R•] can be described to

$$[\text{R}\bullet] = \frac{R_i^{1/2}(k_p[\text{RH}] + k_{t_1}^{1/2}R_i^{1/2})}{k_p k_{t_3}^{1/2}[\text{RH}] + k k_{t_1}[\text{O}_2] + (k_{t_1} k_{t_3} R_i)^{1/2}} \quad (6)$$

Combining Eqs. (1) and (6), and the O₂ decrease rate equation, $-d[\text{O}_2]/dt$, is

$$-\frac{d[\text{O}_2]}{dt} = \frac{k[\text{O}_2]R_i^{1/2}(k_p[\text{RH}] + k_{t_1}^{1/2}R_i^{1/2})}{k_p k_{t_3}^{1/2}[\text{RH}] + k k_{t_1}[\text{O}_2] + (k_{t_1} k_{t_3} R_i)^{1/2}} \quad (7)$$

Given that the chain length is long enough; that is, $k_p[\text{RH}] \gg k_{t_1}^{1/2}R_i^{1/2}$, Eq. (7) is rewritten to

$$-\frac{d[\text{O}_2]}{dt} = \frac{k k_p[\text{O}_2][\text{RH}]R_i^{1/2}}{k_p k_{t_3}^{1/2}[\text{RH}] + k k_{t_1}[\text{O}_2]} \quad (8)$$

Additionally, based on the assumption that the rate of Eq. (R5) is slower in terms of the heterogeneous reaction, Eq. (8) is transcribed into

$$-\frac{d[\text{O}_2]}{dt} = k[\text{O}_2] \left(\frac{R_i}{k_{t_3}} \right)^{1/2} \quad (9)$$

In this way, the O₂ decrease rate equation is expressed by the first-order reaction for O₂.

3.2. Reaction of NC with O₂

3.2.1. O₂ decrease behavior

When NC was stored under dry air, the overall pressure did not change for 3 h, and then the pressure gradually decreased (Fig. 2). A pressure decrease of approximately 4×10^{-3} MPa was observed after 8 h, and then the pressure slowly rose. An analysis of the gas composition by gas chromatography showed that the pressure change was due to a decrease of the O₂ partial pressure.

3.2.2. Kinetic study

In Fig. 3, the O₂ conversion and the heat conversion showed a similar behavior. The O₂ conversion was represented as $1 - [\text{O}_2]/[\text{O}_2]_0$. $[\text{O}_2]_0$ was expressed as initial pressure of O₂. The heat conversion was obtained by dividing the reaction heat by the overall reaction heat as shown in Eq. (10). The heat generation was accompanied by an O₂ decrease. In the experiments, the plot of $-\ln([\text{O}_2]/[\text{O}_2]_0)$ had a linear relationship with the storage time as shown in Fig. 4. Therefore, the O₂ decreasing behavior was of the first order. The heat release behavior was also represented by the first-order reaction. When the heat conversion was denoted as x , the plot of $-\ln(1 - x)$ against storage time had a linear relationship with the correlation coefficient of 0.999 as shown in Fig. 4. The first-order reaction constant (K ; see Eq. (11)) and the induction period (t_{indc}) almost coincided with those of the O₂ conversion (Table 1):

$$\text{heat conversion } (x) = \frac{\int_{t_0}^t q(t) dt}{\int_{t_0}^t q(t) dt} = \frac{\int_{t_0}^t q(t) dt}{\Delta H} \quad (10)$$

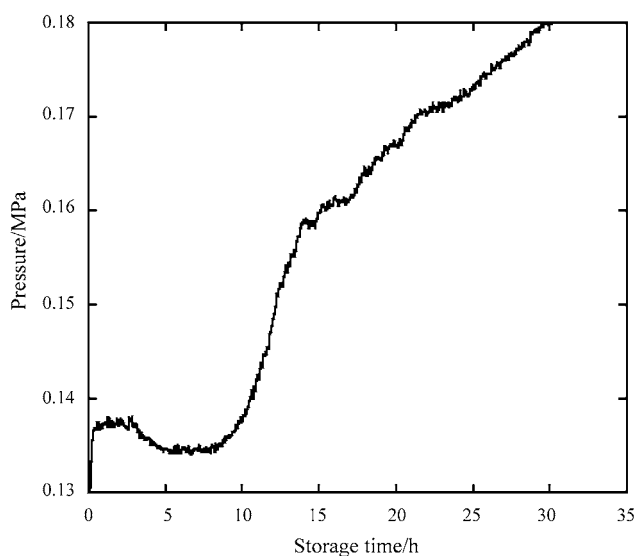


Fig. 2. The overall pressure change during the storage. Storage temperature: 393 K; atmosphere: dry air; initial pressure: 0.1 MPa at room temperature; initial amount of NC: 50 mg.

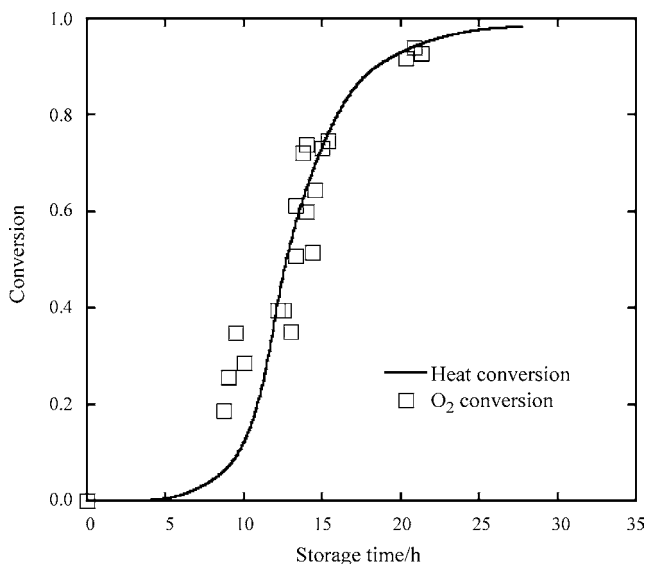


Fig. 3. The O₂ conversion and the heat conversion against the storage time. Storage temperature: 393 K; atmosphere: dry air; initial pressure: 0.1 MPa at room temperature; initial amount of NC: 50 mg.

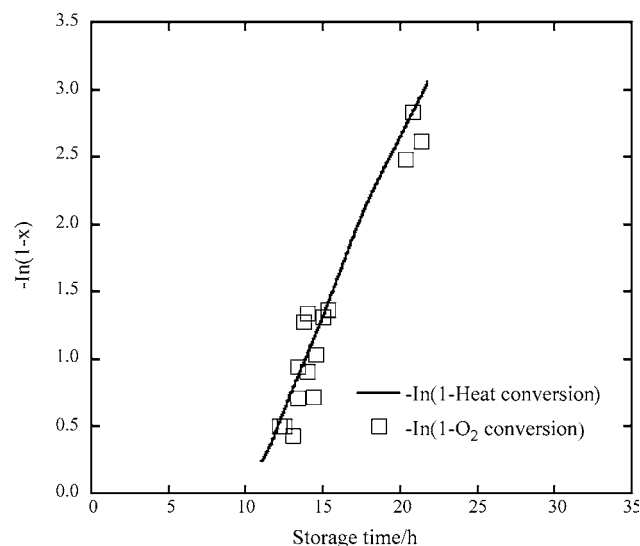


Fig. 4. $-\ln(1-x)$ vs. storage time. Storage temperature: 393 K; atmosphere: dry air; initial pressure: 0.1 MPa at room temperature; initial amount of NC: 50 mg.

Table 1
Comparison between O₂ decrease behavior and heat release behavior

	Amount of reaction heat (J g ⁻¹)	First-order rate constant (s ⁻¹)	Induction period (h)
O ₂ decrease behavior under dry air		7.7×10^{-5}	10
Thermal behavior under dry air			
Integral calculus	460	8.1×10^{-5}	9.2
Van't Hoff's differential calculus		7.7×10^{-5}	
Thermal behavior under 4.7 vol.% NO ₂ /air			
Integral calculus	450	1.8×10^{-4}	3.4
Van't Hoff's differential calculus		1.5×10^{-4}	

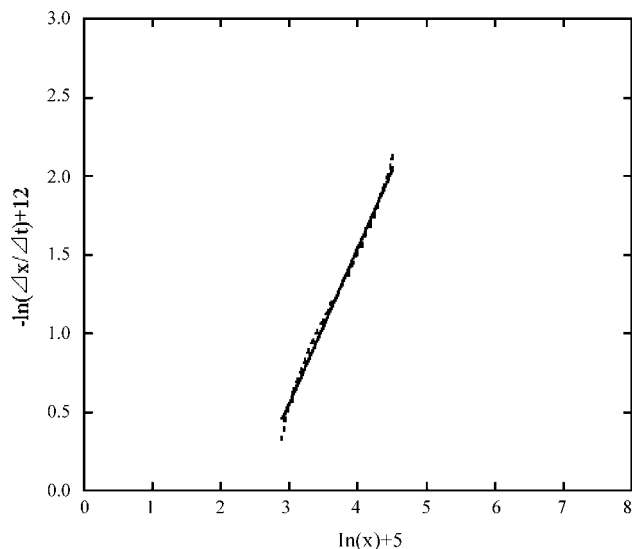


Fig. 5. $\ln(-\Delta x/\Delta t)$ vs. $\ln x(t)$. Solid line: plot of $\ln(-\Delta x/\Delta t)$ vs. $\ln x(t)$; broken line: approximated curve; storage temperature: 393 K; atmosphere: dry air; initial pressure: 0.1 MPa at room temperature; initial amount of NC: 50 mg.

where t is the storage time, t_0 the origin-point of reaction, and t_f is the end-point of reaction.

$$-\ln\left(\frac{[\text{O}_2]}{[\text{O}_2]_0}\right) = Kt, \quad K = k\left(\frac{R_i}{k_{t_3}}\right)^{1/2} \quad (11)$$

The result of Van't Hoff's differential calculus, which was another method in order to investigate a reaction order, indicated the plot of $\ln(\Delta x/\Delta \text{storage time})$ against $\ln(x)$ had a linear relationship with a slope of 0.97, and the correlation coefficient was 0.992 (Fig. 5). The heat release behavior was represented by a first-order reaction since this result corresponded to a first-order equation (Eq. (12)). K obtained by Van't Hoff's differential calculus well agreed with that by integral calculus (Table 1):

$$-\ln\frac{d[\text{O}_2]}{dt} = \ln[\text{O}_2] + \ln K, \quad K = \left(\frac{R_i}{k_{t_3}}\right)^{1/2} \quad (12)$$

The O₂ decrease behavior and the heat release behavior could be explained by an autoxidation mechanism which was also a first-order reaction with respect to the O₂ decrease.

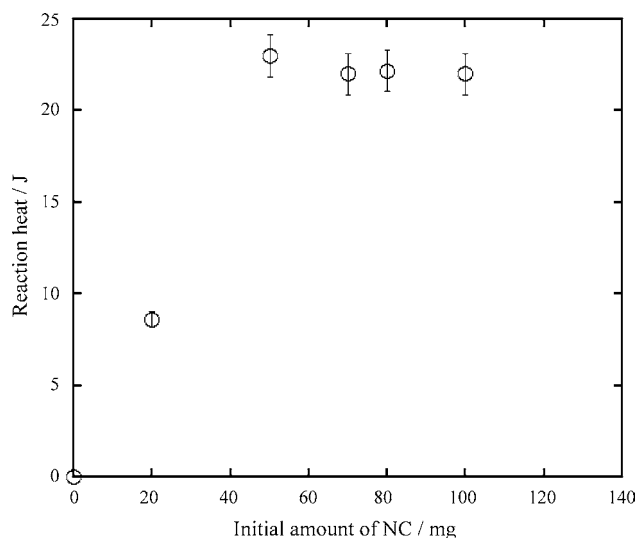


Fig. 6. The relationship between the amount of reaction heat and the initial amount of NC. Storage temperature: 393 K; atmosphere: dry air; initial pressure: 0.1 MPa at room temperature.

3.2.3. Effects of initial amount of NC and initial partial pressure of O_2

The amount of reaction heat did not increase although the initial amount of NC increased from 50 to 100 mg (Fig. 6). On the other hand, the reaction heat of 50 mg of NC increased with the O_2 partial pressure (Fig. 7). These results showed that the amount of reaction heat depended on the O_2 partial pressure, and not the amount of NC. These behaviors would support the autoxidation was involved in the heat release. In Fig. 7, the reaction heat became constant above 0.08 MPa of the O_2 partial pressure. This indicated that the amount of NC needed at least 0.08 MPa of the O_2 partial pressure to complete oxidation.

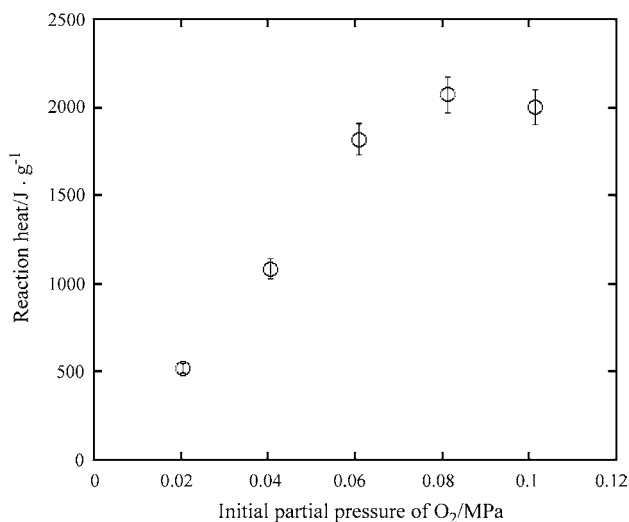


Fig. 7. The relationship between the amount of reaction heat and the initial partial pressure of O_2 . Storage temperature: 393 K; initial amount of NC: 50 mg; initial pressure: 0.1 MPa at room temperature.

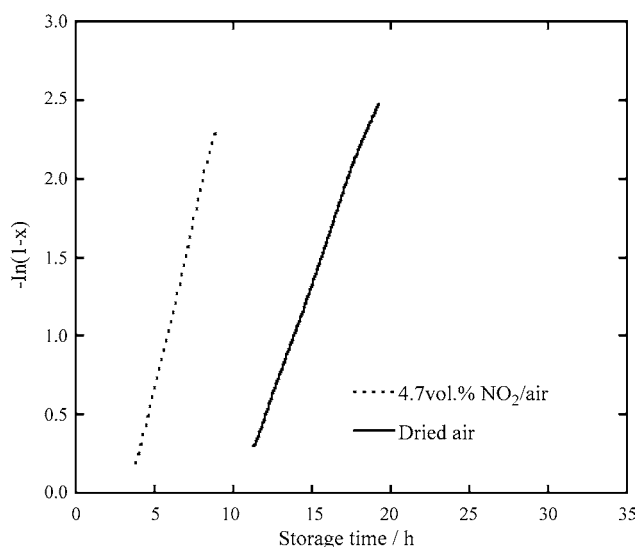


Fig. 8. $-\ln(1-x)$ vs. storage time under the storage in dry air and 4.7 vol.% NO_2 /air. Storage temperature: 393 K; initial pressure: 0.1 MPa at room temperature; initial amount of NC: 50 mg

3.3. Reaction of NC with NO_2

3.3.1. Kinetic study

In 4.7 vol.% NO_2 /air, NC released about the same amount of heat as in dry air. The heat flow behavior in 4.7 vol.% NO_2 /air was similar to that in the dry air. The plot of $-\ln(1-x)$ had a linear relationship with the storage time in 4.7 vol.% NO_2 /air (Fig. 8), and the correlation coefficient was 0.999. Similarly, the plot of $\ln(\Delta x/\Delta t)$ against $\ln(x)$ had a linear relationship with 0.992 of the

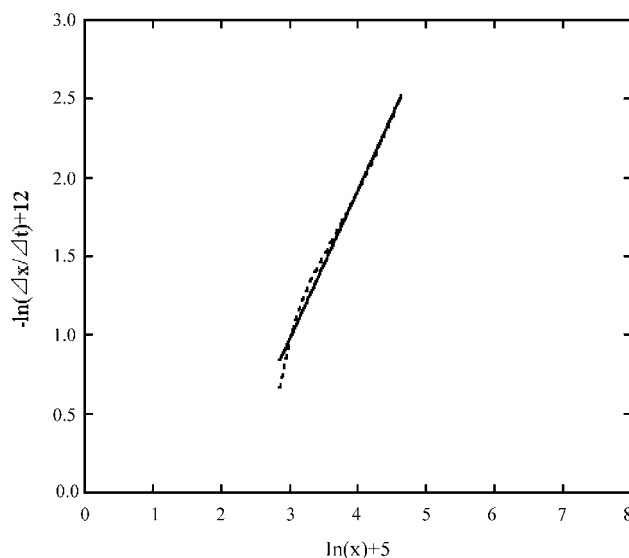


Fig. 9. $-\ln(\Delta x/\Delta t)$ vs. $\ln x$. Solid line: plot of $-\ln(\Delta x/\Delta t)$ vs. $\ln x$; broken line: approximated curve; storage temperature: 393 K; atmosphere: 4.7 vol.% NO_2 /air; initial pressure: 0.1 MPa at room temperature; initial amount of NC: 50 mg.

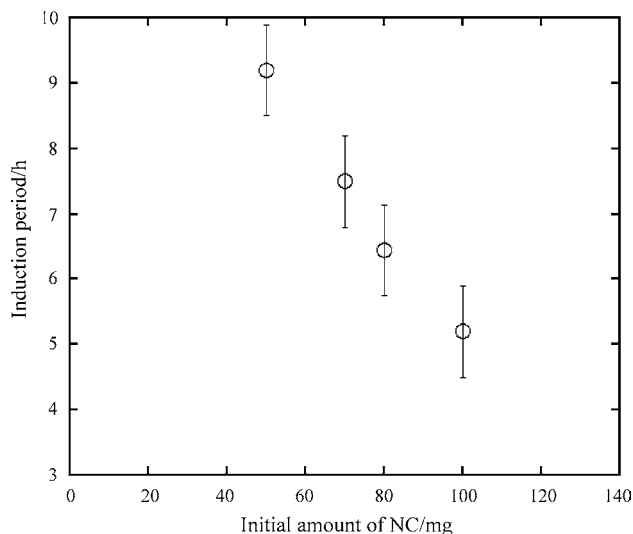


Fig. 10. The relationship between the induction period (t_{indc}) and the initial amount of NC. Storage temperature: 393 K; initial pressure: 0.1 MPa at room temperature; initial partial pressure of O_2 : 0.02 MPa; t_{indc} : the intersection of line in plot of $-\ln(1-x)$ vs. storage time and $-\ln(1-x)=0$

correlation coefficient, and its slope was 0.92 (Fig. 9). These results indicated that the heat release behavior of NC in 4.7 vol.% NO_2/air was expressed by a first-order reaction as well as that in dry air. NO_2 would hardly affect the propagation process since NO_2 did not affect the reaction order.

The t_{indc} value in 4.7 vol.% NO_2/air was shorter than that in dry air, and the K in 4.7 vol.% NO_2/air was slightly larger than that in dry air (Table 1). The hydrogen-abstract rate became higher during the initiation process due to higher NO_2 partial pressure, and the alkyl radical concentration further increased. Therefore, NO_2 would play an important role in the initiation process, but NO_2 hardly contributed to heat generation processes such as the propagation process.

3.3.2. Effect of initial amount of NC

With an increase of the initial amount of NC (20, 40, 50, 70, 80, 100 mg), the t_{indc} decreased (Fig. 10), and the K increased (Fig. 11) in dry air, whereas, the amount of reaction heat did not change. These results were thought to suggest that the initiation process was accelerated by the NO_2 which was increased with the amount of NC.

3.4. Reaction of O_2 with NO

The thermal behavior under different partial pressure of O_2 indicated that the t_{indc} decreased with an increase of the O_2 initial pressure (Fig. 12). This showed the initiation process would be accelerated with an increase of the initial pressure of O_2 . Volltrauer and Fontijn [15] and Nakamura and coworkers [16] suggested that NO was the major component in gases evolved from NC. The reaction described in Eq. (R10) (re-

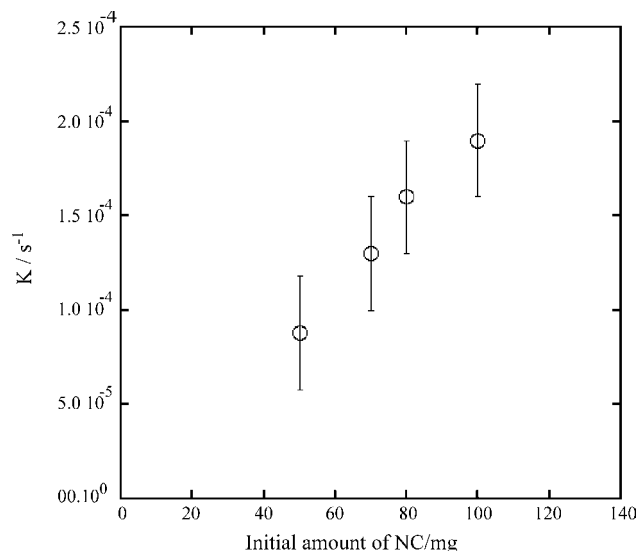


Fig. 11. The relationship between the first-order rate constant (K) and the initial amount of NC. Storage temperature: 393 K; initial pressure: 0.1 MPa at room temperature; initial partial pressure of O_2 : 0.02 MPa; K : the inclination of line in plot of $-\ln(1-x)$ vs. storage time.

action between NO and O_2) might play an important role in terms of the NO_2 generation.

However, the reaction between O_2 and NO (Eq. (R10)) hardly contributed to the O_2 decrease. Atkinson et al. [17] reported that a reaction constant, $k_{\text{NO} \rightarrow \text{NO}_2}$, of Eq. (R10) was $2.19 \times 10^{-38} \text{ mol}^{-2} \text{ cm}^6 \text{ s}^{-1}$. Kawaguchi et al. [18] estimated that the NO generation rate of NC was approximately $1.7 \times 10^9 \text{ mol cm}^{-3} \text{ s}^{-1}$ per 50 mg NC at 338 K. If [NO] in Eq. (13) was constant at the NO concentration after 24 h, the pseudo-first-order constant ($k[\text{NO}]^2$) was estimated to be $4.2 \times 10^{-10} \text{ s}^{-1}$. This value

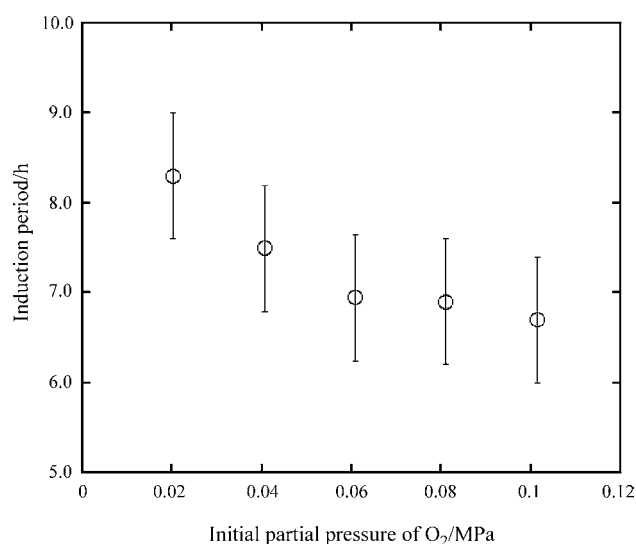


Fig. 12. The relationship between the induction period (t_{indc}) and the initial partial pressure of O_2 . Storage temperature: 393 K; initial pressure: 0.1 MPa at room temperature; initial amount of NC: 50 mg; t_{indc} : intersection of a tangent on the maximum inclination point of heat flow and heat flow = 0.

was adequately lower than K in the present study. In addition, the rate of Eq. (R10) will become lower because Eq. (R10) is equilibrium reaction. These indicated that Eq. (R10) did not significantly participate in the O_2 decrease reaction:



$$-\frac{d[O_2]}{dt} = k_{NO \rightarrow NO_2} [NO]^2 [O_2] \quad (13)$$

4. Conclusion

The spontaneous ignition mechanism of NC was analyzed in terms of the pressure change and the thermal behavior during isothermal storage (393 K).

During the storage of NC, atmospheric O_2 was consumed in an exothermic reaction. The heat release behavior of NC as well as the O_2 decreasing behavior could be fitted to a first-order reaction, which would suggest autoxidation. The value of K and t_{indc} for the O_2 decreasing behavior almost coincided with those for the heat release behavior. The reaction heat did not increase even if the initial amount of NC increased in a limited O_2 environment. These results would suggest that autoxidation was involved in the heat release of NC.

Even in 4.7 vol.% NO_2 /air, the amount of the reaction heat did not significantly change from that in dry air. The reaction order was also not affected by the partial pressure of NO_2 . On the other hand, the K was larger, and the t_{indc} was shorter in 4.7 vol.% NO_2 /air than those in dry air. These results indicated that NO_2 contributed to the initiation process rather than following autoxidation.

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