

Thermal decomposition behavior of nitrocellulose mixed with acid solutions

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Abstract

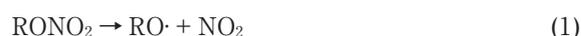
In this investigation, the thermal decomposition behaviors of nitrocellulose (NC) and its mixtures with H₂SO₄, HNO₃, or HCl solutions were observed under controlled ramp heating and isothermal conditions. The exothermic peak temperature (T_p) for NC/H₂SO₄, determined by differential scanning calorimetry (DSC) under different heating conditions, was the lowest among the examined samples. The thermal behavior of NC/HNO₃ was strongly influenced by the heating rate; T_p was similar to that of NC alone at the heating rates of 3–5 °C·min⁻¹, whereas it was lower than that of NC alone at heating rates lower than 1 °C·min⁻¹. Furthermore, heat flux calorimetry analysis of the thermal behavior under isothermal conditions at 70 °C revealed that the induction period for the exothermic decomposition (t_p) of NC/HNO₃ was the shortest among the examined samples. Thus, not only H₂SO₄ but also HNO₃ is thought to remarkably accelerate the thermal decomposition of NC. On the contrary, HCl did not show any reactivity toward NC, as T_p and t_p for NC/HCl were almost the same as those for NC alone, regardless of the heating rate. In addition, when the kinetic parameters for each sample were calculated using DSC data at different heating rates, a linear relationship between the activation energy and the logarithm of the frequency factor was established for NC/HNO₃, NC/HCl, and NC alone, indicating that a compensation effect was established for these samples. In contrast, the data corresponding to NC/H₂SO₄ was not located on the same line. Thus, the decomposition mechanism of NC/H₂SO₄ is suggested to be different from that of the other samples.

Keywords: nitric acid ester, spontaneous ignition, thermal stability, calorimetry

1. Introduction

Nitrocellulose (NC), which is synthesized from cellulose (generally, cotton linter) and a mixed acid (H₂SO₄ and HNO₃), is an industrially useful material that is utilized as the starting material for lacquers, celluloid products, and explosives. However, NC is an unstable material that presents the risk of spontaneous ignition, even at low temperatures, and numerous accidental explosions resulting from its ignition have been reported^{(1)–(9)}. In general, NC is suggested to spontaneously ignite through the accumulation of the heat of self-decomposition. The

initial decomposition involves the following reactions⁽¹⁰⁾ :



Equation (1) describes thermal bond scission of O–NO₂ and Equation (2) describes the hydrolysis of the ONO₂ group. According to a previous study⁽¹¹⁾, water vapor destabilizes NC by accelerating the hydrolysis, whereas liquid water stabilizes NC by absorbing the heat of decomposition. The hydrolysis of NC occurs autocatalytically; it is catalyzed by HNO₃ generated

during the hydrolysis and residual H_2SO_4 used in the synthetic process¹⁰. Thus, hydrolysis proceeds exponentially, once HNO_3 is generated. Besides these reactions, the reaction between NC and H_2SO_4 is suggested to generate sulfuric esters, which are active species that accelerate the decomposition of NC¹².

Therefore, acids like H_2SO_4 and HNO_3 strongly contribute to the decomposition and spontaneous ignition of NC, although the actual degradation mechanism is likely to be more complex, involving reactions such as atmospheric oxidation^{13,14} and the formation of active species other than sulfuric esters^{15,16}. Thus, previous studies^{12,17,19,20} have focused on the thermal stability of mixtures of NC and acids. However, we noticed discrepancies in previous studies^{12,17,19,20}, in terms of the degree of destabilization achieved by different types of acids. For example, Osada¹² reported that the thermograms of NC/ HNO_3 and NC/ HCl mixtures under controlled ramp heating conditions were similar to those of NC alone and NC containing a stabilizer, whereas the peak and onset temperatures of NC/ H_2SO_4 were observed to decrease by at least 100 °C, suggesting that NC was destabilized exclusively by H_2SO_4 . Another study reported by Demougin and Landon¹⁷ and reviewed by Urbanski¹⁸ indicated that among various acids, H_2SO_4 influenced the thermal stability of NC to the greatest extent, with the destabilizing effect increasing in the order, $\text{HNO}_3 < \text{HCl} < \text{H}_2\text{SO}_4$. Furthermore, according to a previous study by Khrapkovskii *et al.*¹⁹, H_2SO_4 destabilizes NC much more than HNO_3 . In contrast, Nakamura *et al.*²⁰ carried out thermal analysis under controlled ramp heating and isothermal conditions, and reported that the thermal stability of NC in the presence of an acid mixture (HNO_3 and H_2SO_4) decreased as the HNO_3 ratio in the mixture increased, suggesting that HNO_3 contributed dominantly to the decomposition of NC.

Clearly, the reactions between NC and acids are critical in terms of the explosion safety of NC. However, as described above, there is no clear understanding of which of the acids positively contribute to the decomposition of NC. In order to rationalize the inconsistencies in the previous studies^{12,17–20}, we speculated that the reactivity between NC and acids varies according to the evaluation or experimental conditions (e.g., heating conditions, sample conditions, sample container volume, sample scale, and the amount and concentration of the acid solution). In this study, we focused on the heating conditions by investigating the thermal behavior of NC alone and NC mixed with acid solutions under various heating rates, as well as under isothermal conditions, using differential scanning calorimetry (DSC) and heat flux calorimetry (C 80) that are widely used as hazard evaluation methods^{21,22}.

2. Experimental

2.1 Materials

NC (N% = 12.5) provided by NOF Corp. was dried under vacuum at ambient temperature for more than three days before using as the experimental sample. H_2SO_4 and HNO_3

that are used as reactants in the synthesis of NC were employed as acid components. HCl was also used as an additive although it is not mixed with NC in industrial processes. Solutions of these three acids were prepared at a concentration of $2.3 \text{ mol}\cdot\text{L}^{-1}$ by diluting the commercial reagents (Wako Pure Chemical Industries, Ltd.) with purified water.

2.2 DSC measurements

Each diluted acid solution (2.5 mg) was added to dry NC (10 mg) and each sample was mixed well using a bamboo skewer in a glass tube. An aliquot of the sample (0.2 mg) was placed in a cylindrical container (Seiko Instruments Inc.; material: SUS; capacity: 15 μL), which was subsequently sealed. The DSC measurements were conducted using a DSC3100 instrument (Mac Science Corp.) at heating rates between $0.2\text{--}5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ in the temperature range of $20\text{--}280 \text{ }^\circ\text{C}$.

2.3 C80 measurements

Dry NC (35 mg) was placed in a glass container, and each acid solution (8.9 mg) was added to the container. Each sample was mixed well as described for the DSC samples. The glass container with the sample was inserted into a cylindrical container (Rigaku Corp.; material: SUS; spatial volume: $\sim 4 \text{ mL}$), which was subsequently sealed. Heat flux calorimetry measurements were performed using a C80 calorimeter (Setaram Instrumentation), under isothermal conditions at $70 \text{ }^\circ\text{C}$.

3. Results and discussion

3.1 Thermal behavior under different heating conditions

Figure 1 shows the DSC thermograms under a heating rate of $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ for NC/ H_2SO_4 , NC/ HNO_3 , and NC/ HCl , and for NC alone serving as a reference. The peak temperature (T_p) for NC/ H_2SO_4 was observed at $124 \text{ }^\circ\text{C}$, which is approximately $80 \text{ }^\circ\text{C}$ lower than that for NC alone ($T_p = 203 \text{ }^\circ\text{C}$). In the cases of NC/ HNO_3 and NC/ HCl , no change in T_p was observed relative to that of NC, and the shapes of the exothermic peaks were also similar. This behavior is consistent with that reported by Osada¹². From this data, only H_2SO_4 appears to affect the thermal stability of NC. However, as shown in Figure 2, the thermal behavior of NC/ HNO_3 changed at lower heating rates ($0.2 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$), with T_p observed at $118 \text{ }^\circ\text{C}$, which is lower than that of NC alone ($T_p = 171 \text{ }^\circ\text{C}$). Thus, not only H_2SO_4 but also HNO_3 plays a prominent role in NC decomposition. On the other hand, T_p and the shape of the exothermic peak for NC/ HCl were similar to those of NC alone at both heating rates (0.2 and $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$).

Similar measurements were conducted at different heating rates ($0.2\text{--}5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$) to determine the kinetic parameters. Figure 3 shows the relationship between $\ln(\beta/T_p^2)$ and $1/T_p$ based on the Kissinger equation (Equation (3))²³. Further, the activation energies (E_a) derived from the slopes in Figure 3 and the frequency factors (Z) calculated using Equation (4)²⁴ are provided in Table 1.

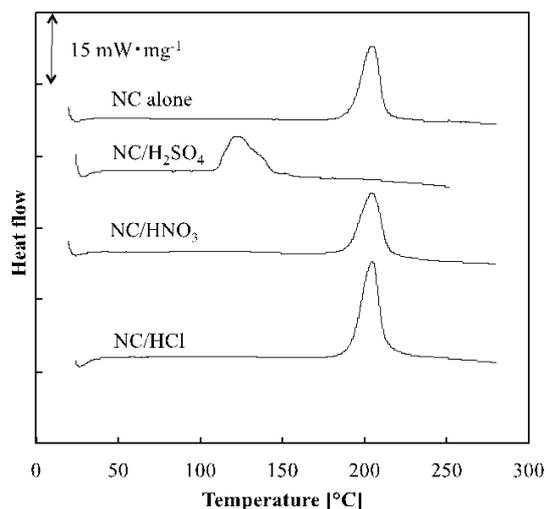


Figure 1 DSC thermograms of NC and its mixtures with acid solutions at a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

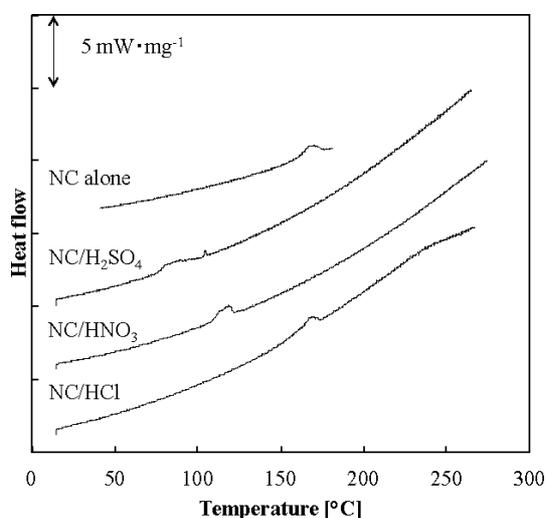


Figure 2 DSC thermograms of NC and its mixtures with acid solutions at a heating rate of $0.2\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

$$E_a = -R \left[\frac{d \ln(\beta/T_p^2)}{d(1/T_p)} \right] \quad (3)$$

$$Z = \frac{\beta \cdot E_a \cdot \exp(E_a/R \cdot T_p)}{R \cdot T_p^2} \quad (4)$$

where, β is the heating rate and R is the gas constant. In addition, E_a and Z were calculated using AKTS-thermokinetics software^{(25), (26)} based on the Friedman equation (Equation (5))⁽²⁷⁾.

$$\ln \frac{d\alpha}{dt} = \ln[Z \cdot f(\alpha)] - \frac{E_a(\alpha)}{R \cdot T} \quad (5)$$

where, α , t , $f(\alpha)$, R , and T are the heat conversion, time, reaction model, gas constant, and temperature, respectively. Provided that $f(\alpha)$ is constant under the same heat conversion, E_a and Z corresponding to various α values can be calculated as shown in Figure 4 and Table 1.

From the kinetic analysis, it is obvious that E_a corresponding to the heating rate dependence on exothermic decomposition is different for each of the added acids. NC/HNO₃ was most influenced by the

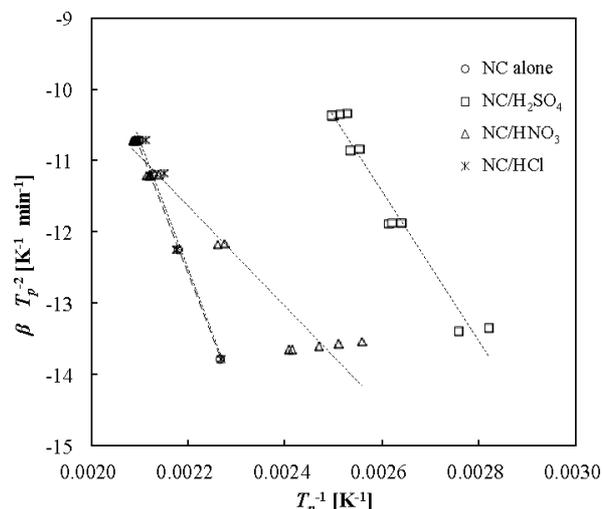


Figure 3 Kissinger plots of NC and its mixtures with acid solutions based on DSC results.

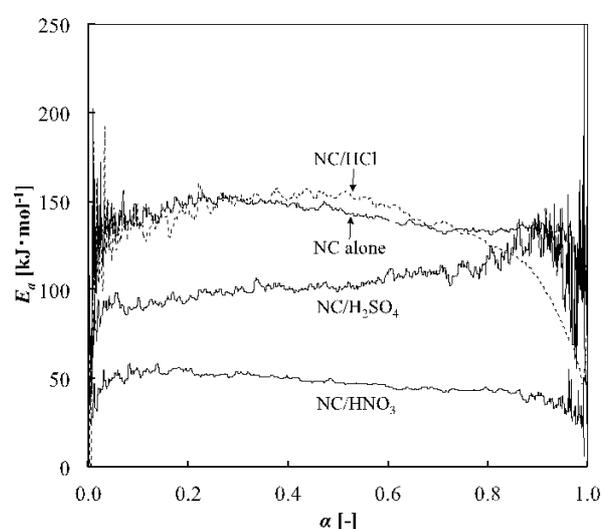


Figure 4 Relationship between E_a and α calculated by the Friedman method based on DSC results under heating conditions.

Table 1 Kinetic parameters for decomposition of NC and its mixtures with acid solutions.

	Kissinger		Friedman*	
	E_a [kJ·mol ⁻¹]	$\ln Z$ [min ⁻¹]	E_a [kJ·mol ⁻¹]	$\ln Z f(\alpha)$ [min ⁻¹]
NC alone	147	36	145	32
NC/H ₂ SO ₄	87	25	99	25
NC/HNO ₃	58	12	48	6.6
NC/HCl	150	37	152	33

*The values at $\alpha = 0.5$

heating rate, and thus, the lowest E_a value was observed. In addition, E_a for NC/H₂SO₄ was lower than that for NC alone. The kinetic parameters of NC/HCl were very similar to those of NC alone. Notably, the E_a value for NC/HNO₃ is similar to that for NC alone for heating rates in the range of $3\text{--}5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ (Figure 3), which indicates that the evaluation of the reactivity of NC/HNO₃ would be incorrect when judged only from DSC thermograms obtained under a high heating rate.

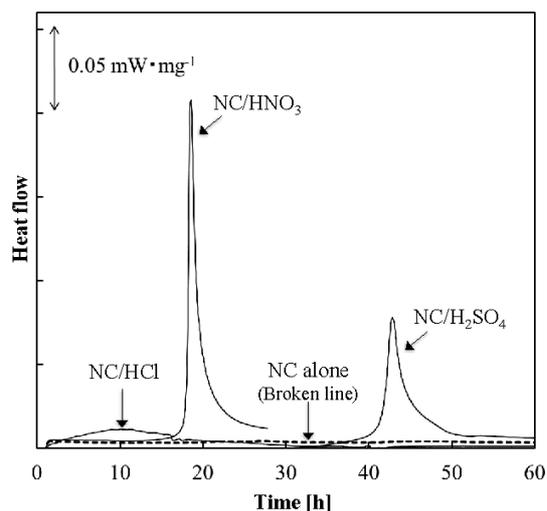


Figure 5 Thermograms of NC and its mixtures with acid solutions measured using a C80 calorimeter under isothermal conditions at 70 °C.

3.2 Thermal behavior under isothermal conditions

The thermal behaviors of NC alone, NC/H₂SO₄, NC/HNO₃, and NC/HCl were also evaluated under isothermal conditions at 70 °C using a C80 calorimeter. As shown in Figure 5, an exothermic peak was observed for NC/H₂SO₄ and NC/HNO₃. As an exothermic peak was not observed for NC alone, we suggest that H₂SO₄ and HNO₃ accelerated NC decomposition, similar to the above-mentioned behavior observed under heating conditions used in DSC. Further, the induction time for the exothermic peak (t_p) in NC/HNO₃ (19 h) was shorter than that for NC/H₂SO₄ (t_p = 43 h). This difference possibly corresponds to the lower value of E_a for NC/HNO₃ observed by DSC. Thus, depending on the reaction conditions, HNO₃ can destabilize NC more than H₂SO₄, although previous studies^{12),17–19)} have indicated that H₂SO₄ has the greatest influence on the thermal stability of NC. For NC/HCl, a weak exothermic peak was observed 10 h after storage. This exothermic peak likely does not correspond to the heat of decomposition of NC; instead, it corresponds to the reaction between the sample container and vaporized HCl, because a similar exothermic peak was observed during C80 measurements of HCl alone.

Figure 6a shows the thermograms calculated from the Friedman analysis based on the DSC measurements, whereas Figure 6b shows the experimental thermograms obtained under isothermal conditions at 70 °C. Comparison of the calculated and experimental thermograms indicates that the estimated t_p values for both NC/H₂SO₄ and NC/HNO₃ are shorter than the experimental values. This difference may be related to the vapor–liquid equilibrium of water in the acid solutions. That is, as the estimated thermogram (Figure 6a) is based on DSC measurements at 100 °C or higher, the added acid solution was concentrated owing to the vaporization of water. On the contrary, during the C80 measurements at 70 °C, more water remained in the liquid phase in NC. In a previous study¹¹⁾, we reported that liquid water stabilizes NC by absorbing the heat of decomposition. Therefore, we suggest that the estimated t_p values for both NC/H₂SO₄

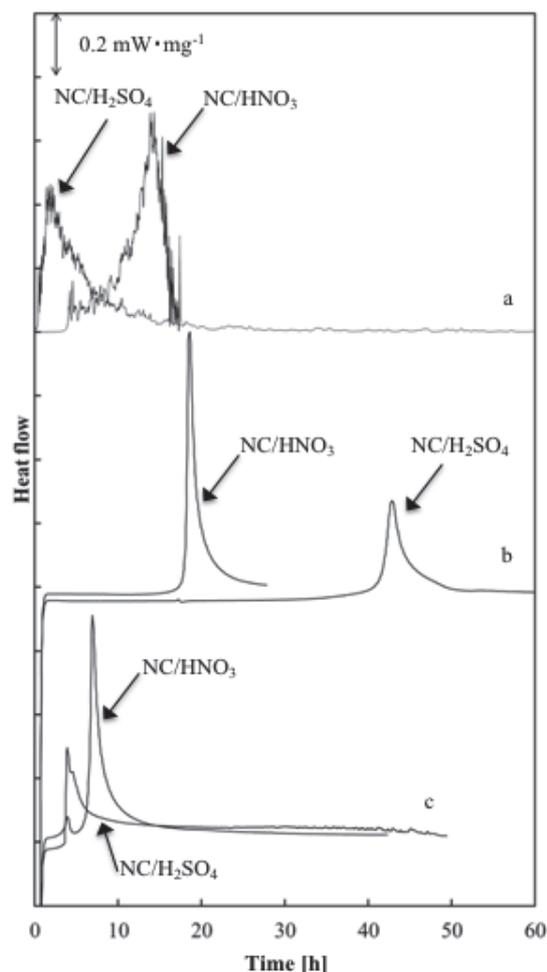


Figure 6 Thermograms of NC/H₂SO₄ and NC/HNO₃ under isothermal conditions at 70 °C (a: results of calculation based on the Friedman method using DSC data, C80 results for NC (35 mg) containing an acid solution; b: 2.3 mol·L⁻¹, 8.9 mg; and c: 6.6 mol·L⁻¹, 3.3–3.6 mg).

and NC/HNO₃ are shorter than the experimental values. To confirm this hypothesis, the thermal behavior of NC containing higher concentrations of H₂SO₄ and HNO₃ (i.e., low water contents) was examined. Under these conditions (Figure 6c), the t_p values were shorter than those at a lower concentration, and the t_p values roughly agreed with those observed in the thermogram estimated from the kinetic analysis, which is consistent with the above-described hypothesis.

3.3 Decomposition mechanism

In the previous section, the E_a values of both NC/H₂SO₄ and NC/HNO₃ were observed to be lower than that of NC alone. In addition, the kinetic parameters in Table 1 reveal that Z is also different for each mixture with a different type of acid. Figures 7 and 8 show the relationship between E_a and the logarithm of Z , as analyzed by the Kissinger and Friedman methods. As revealed by these figures, a good linear relationship is found in the plots of NC/HNO₃, NC/HCl, and NC alone, regardless of the analytical method, which indicates that a compensation effect²⁸⁾ was established in case of these three samples. On the other hand, the NC/H₂SO₄ data does not fall on the same compensation line. A previous study¹⁴⁾ suggested

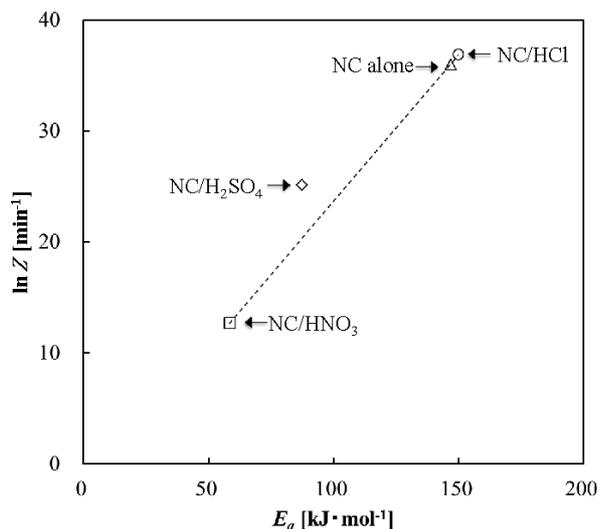


Figure 7 Relationship between $\ln Z$ and E_a calculated by the Kissinger method.

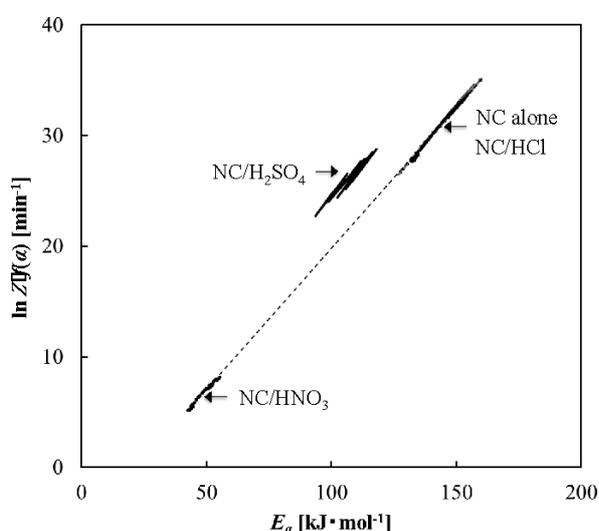


Figure 8 Relationship between $\ln Z$ and E_a calculated by the Friedman method.

that the compensation line differs depending on the reaction model or measurement apparatus. This study reveals that the type of the acid added to NC also changes the compensation line.

In addition, according to previous studies^{29,30}, when a compensation effect is established, the reaction occurs via the same mechanism. Thus, it is possible that the decomposition of NC/HNO₃, NC/HCl, and NC alone occurs by similar mechanisms, whereas the decomposition of NC/H₂SO₄ occurs via a different pathway. This result may indicate that NC/HCl would decompose via thermal bond scission (Equation (1)), hydrolysis (Equation (2)), and subsequent reactions between NC and NO₂, similar to NC alone, since HCl does not participate in the NC decomposition. Provided the decomposition promotion by HNO₃ results from the catalytic effect for the hydrolysis or from the increase in the NO_x amount by the addition of HNO₃, the mechanism underlying the decomposition of NC/HNO₃ should be the same as that for NC and NC/HCl. In contrast, for NC/H₂SO₄, a previous study¹² suggested that thermally active substances like sulfuric esters are generated by reactions between NC and H₂SO₄. As these

reactions cannot take place in the absence of H₂SO₄, like in the case of NC alone and other acid mixtures, the compensation effect might only be different in the case of NC/H₂SO₄. Khrapkovskii et al.¹⁹ reported that the thermal decomposition of NC is determined by the hydrolysis of NC by H₂SO₄. However, since H₂SO₄ accelerates the hydrolysis, the same compensation effect should be established in NC/H₂SO₄ and other samples, which contradicts the results depicted in Figures 7 and 8. Therefore, the contribution of the hydrolysis catalyzed by H₂SO₄ is speculated to be comparatively small, at least under the experimental conditions employed in this study.

4. Conclusions

In this study, the thermal behaviors of mixtures of NC and H₂SO₄, HNO₃, or HCl were evaluated at various heating rates and under isothermal conditions at 70 °C using DSC and C80 measurements. Furthermore, the reactivity of each acid was investigated and compared with that of NC alone. The following conclusions can be drawn from the results :

- The exothermic peak temperature (T_p) and the induction time for the exothermic peak (t_p) for NC/H₂SO₄ and NC/HNO₃ decreased at lower heating rates (less than 1–3 °C·min⁻¹) and under isothermal conditions in comparison with those of NC alone. On the other hand, the thermal behavior of NC/HCl was the same as that of NC alone under every heating condition examined in this study. Thus, H₂SO₄ and HNO₃ are suggested to accelerate the decomposition of NC, whereas HCl does not react with NC.
- The E_a values of NC/HNO₃ calculated by the Kissinger and Friedman methods using DSC data were the lowest among the examined samples, which suggests that the decomposition rate of NC/HNO₃ is strongly influenced by the heating rate. Consequently, the thermal behavior of NC/HNO₃ is similar to that of NC alone at the heating rates of 1–3 °C·min⁻¹, whereas T_p and t_p of NC/HNO₃ decreased remarkably in comparison with those of NC alone at heating rates less than 1 °C·min⁻¹.
- Investigation of the relationship between E_a and $\ln Z$ revealed that the data for each parameter corresponding to NC/HNO₃, NC/HCl, and NC alone fall on a linear line, whereas those of the NC/H₂SO₄ deviate from the lines. Thus, it can be suggested that the degradation of NC occurs through the same mechanism regardless of the absence or presence of HNO₃ and HCl, whereas it occurs via a different reaction pathway in the presence of H₂SO₄.

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