Effects Of Nitric Acid And Sulfuric Acid On Thermal Stability Of Nitrocellulose

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Effects of nitric acid and sulfuric acid on thermal stability of nitrocellulose

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Abstract

Sulfuric acid and nitric acid are two typical impurities in manufacturing, storage, processing, and transportation of nitrocellulose, and may reduce the thermal stability of nitrocellulose and increase hazards. Thermal behaviors of nitrocellulose contaminated by nitric acid and sulfuric acid were explored by a C80 micro calorimeter. Two exothermic processes were observed after adding acids into nitrocellulose. Kinetics and thermodynamics of pure nitrocellulose and its mixture with two acids were obtained by Kissinger method and Ozawa method. The catalytic mechanism was tested by analysis of reaction curve and isothermal experiments. Impurities of nitric acid and sulfuric acid decreased thermal stability of nitrocellulose with different mechanisms.

Keywords: Nitrocellulose; thermal decomposition; impurity; mechanism

Thermal decomposition of nitric acid

Acid hydrolysis of nitrocellulose

Thermal decomposition of nitrocellulose

Hydrolysis of NC

Thermal decomposition of sulfuric acid

Formation of sulfuric acid ester

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17 1. Introduction

18 Nitrocellulose (NC) is a derivative nitro compound obtained by esterification
 19 reaction between natural cellulose ($[\text{C}_6\text{H}_7\text{O}_2(\text{OH})_3]_n$) and nitric acid (NA) [1], in which
 20 part of the hydroxyl groups (-OH) in cellulose are esterified into nitrate ester groups (-
 21 ONO_2) [1]. Due to these groups, NC is an energetic material. And yet it is widely used
 22 in manufacturing of lacquers, photographic film, printing inks, celluloid, and explosives
 23 [2]. NC is stable in room temperature but could easily auto-ignite under high
 24 temperature accompanying by rapid decomposition [3]. Many accidents were caused
 25 by the spontaneous ignition of NC, and a typical example is the 8•12 fire and explosion
 26 accidents occurred in Tianjin Port, China. Besides, in the process of manufacturing,
 27 storage, transportation and practical use, NC is likely to be contaminated by impurities,

such as inorganic acids, organic oil and so on. Contamination of pure chemicals, especially nitro compounds contaminated by impurities may greatly lower the stability, leading to unexpected decomposition and thermal hazards [4].

Previous research has done many works according to the thermal decomposition phenomenon, kinetics, and mechanism of NC. It is generally accepted that decomposition of NC begins by the break of -O-NO₂ and release NO₂ gaseous products which have catalytic effects on the decomposition process [5-7]. However, there have been very few works to explore the effects of acid impurities on thermal behavior of NC. The only accessible work of these authors is carried out by Katoh et al. [8], who applied an ARC (Accelerating Rate Calorimeter) technique to detect the influences of sulfuric acid (SA) on thermal behavior of NC. Their experiments showed that the existence of SA obviously reduced the onset temperature of decomposition and cause rapid explosion [8]. In addition to SA, NA is also a typical impurity in industry. However, there is a blank in comparison of these two impurities in perspective of mechanism, kinetics, and thermodynamics. Hence, a micro calorimeter technique is applied in this study to obtain the thermal behavior of NC contaminated by NA and SA, respectively. The different effects of two acids on thermal stability of NC are compared. The kinetics and thermodynamics are calculated, and the mechanism and hazards are identified.

2. Samples and experiment

2.1 Samples preparation

The experimental samples are coating used nitrocellulose. An Elementar varlo EL produced by Elementar Analysensysteme GmbH (Germany) was applied to determine the nitrogen content, which is 11.76%±0.03%. NA and SA in concentration of 20% were made in laboratory by diluting distilled water into concentrated acids of AR grade. The mass fraction of two acids added in mixture is about 30.32%. Detailed information of all samples is listed in Table 1.

Table 1. Information of experimental samples.

Sample No.	Sample composition	NC mass/mg	Total mass/mg
NC	100% NC	125.9	125.9
NC-NA	30.32% NA, 69.68% NC	128.7	215.7
NC-SA	30.32% SA, 69.68% NC	150.3	184.7

2.2 Experimental apparatus and program

A calvet heat flux calorimeter (C80) manufactured by SETARAM (France) was applied to detect the thermal behavior. It has major merits of high sensitivity with several μW at least and could contain high pressure and large sample mass. Samples were heated from room temperature to 300 °C at heating rates of 0.2, 0.4 and 0.5 °C min^{-1} , respectively. All the isothermal experiments were set to last for 15000s. The sample was sealed in the reaction cell, and reference cell was filled with alumina in the same mass. During all experimental process, normal air atmosphere was applied.

3. Results and discussion

3.1 Effects of acids and heating rate on thermal behavior

Heat flow plots of three samples under heating rates of 0.2, 0.4 and 0.5 °C min^{-1} by C80 micro calorimeter are shown in Fig. 1 (a)~(c). Fig. 1 (d) compares the heat flow plots of three samples under a 0.2 °C min^{-1} heating rate. Based on previous experiences [9], the heat flow plots are analyzed by parameters include onset temperature (T_{on}), peak temperature (T_{m}), and peak heat flow (H_{m}) and so on. Onset temperatures is extrapolated as the temperature at intersection of baseline and tangent to the exothermic peak [10]. Information of the plots in details are listed in Table 2~4.

Fig. 1. Heat flow plots of (a) NC, (b) NC mixed with NA, (c) NC mixed with SA under heating rates of 0.2, 0.4, 0.5 °C min⁻¹.

Table 2. Heat flow characteristics of NC under heating rate of 0.2, 0.4, 0.5 °C min⁻¹.

No.	T_{on} (°C)	ΔT (°C)	H_m (mW g ⁻¹)	T_m (°C)	ΔT_m (°C)	ΔH (J g ⁻¹)
NC-0.2	142.94	3.0	14669.65	143.04	0.02	3799.04
NC-0.4	138.09	4.02	13735.66	138.15	0.06	3620.617
NC-0.5	152.47	4.41	12124.86	152.56	0.11	3131.186

Table 3. Heat flow characteristics (Peak 1) of NC mixed with acids under heating rates of 0.2, 0.4, 0.5 °C min⁻¹.

No.	T_{on} (°C)	ΔT (°C)	H_m (mW g ⁻¹)	T_m (°C)	ΔT_m (°C)	ΔH (J g ⁻¹)
NC-NA-0.2	62.53	57.92	25.12	99.48	36.95	504.21
NC-NA-0.4	75.9	79.27	59.84	106.52	30.62	1019.40
NC-NA-0.5	77.6	71.7	62.31	112.89	35.29	880.51
NC-SA-0.2	124.35	12.67	9491.64	129.72	5.37	4058.09
NC-SA-0.4	126.02	21.7	8908	135.71	9.69	3696.63

NC-SA-0.5	131.22	24.35	9058.92	139.34	8.12	3854.48
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Table 4. Heat flow characteristics (Peak 2) of NC mixed with acids under heating rates of 0.2, 0.4, 0.5 °C min⁻¹.

No.	T_{on} (°C)	ΔT (°C)	H_m (mW g ⁻¹)	T_m (°C)	ΔT_m (°C)	ΔH (J g ⁻¹)
NC-NA-0.2	141.83	21.74	3986.84	154.6	12.77	3125.76
NC-NA-0.4	153.12	18.74	9812.83	162.34	9.22	3887.69
NC-NA-0.5	156.67	20.14	10684.35	164.17	7.5	3986.68
NC-SA-0.2	141.75	36.06	43.13	142.72	0.97	288.39
NC-SA-0.4	150.07	43.54	28.76	150.73	0.66	238.56
NC-SA-0.5	161.17	31.17	-2.36	162.94	1.77	146.29

Heated from room temperature to 300 °C, one exothermic peak was observed in NC. The temperate region was 162~182 °C, with a peak heat flow of 981.42 mW g⁻¹ at temperature of 176 °C. From Fig.1 (b) and (c), two peaks were identified under three heating rates, noted as Peak 1, B for NC mixed with NA and Peak 1', B' for NC mixed with SA. For NC mixed with NA, the first exothermic process ranged from 62.53 °C to 120.45 °C, with peak heat flow of 25.12 mW g⁻¹. Then a much sharper exothermic peak was shown (Peak 2). The initial temperature of Peak 2 moved forward to 141.53 °C, and quickly ended at 163.57 °C. The thermal decomposition process of Peak 2 proceeded more rapidly than sample 1 and reached H_m of 3986.84 mW g⁻¹ at temperature of 154.6 °C. The value of H_m is four times higher than NC. After 154 °C, there were some variations in the heat flow curves, but were insignificant comparing with the H_m . The Peak 1 of NC mixed with NA was very slight and insignificant compared to Peak 2. While for NC mixed with SA, Peak 1' contributed to most of the heat and Peak 2' was very small. NC mixed with SA had the sharpest exothermic peak started at 124.35 °C and promptly reached the highest H_m of 9491.64 mW g⁻¹ at 129.72 °C, over twice higher than the value of NC mixed with NA. Its temperature region for thermal decomposition of Peak 1' ended at 137.02 °C. The onset temperature was

dramatically lower than other samples, and it took much shorter time to reach the peak heat flow. After Peak 1', a secondary Peak 2' was identified from 141.75 to 177.81 °C, which also reached its Peak 1 at 142.72 °C rapidly.

With increase of heating rate, all the heat flow plots moved to a high temperature, and there was an obvious change of T_m and H_m for NC and Peak 2 of NC mixed with NA. The Peak 2 became much sharper and narrower. For the Peak 1' in NC mixed with SA, T_{on} became higher but T_m and H_m were similar, almost reaching the measuring range of the experimental apparatus under three heating rates, indicating a more vigorous exothermic process. The phenomenon of moving towards higher temperature region is caused by the thermos inertia, referring to a relative lag of temperature between samples and apparatus [11]. With a higher heating rate, temperature of samples cannot catch up with furnace temperature, leading to a lag of heat flow plots. So a higher onset temperature and peak temperature were achieved. However, the heat flow plots were in similar shape under various heating rates, indicating that heating rate did not change the reaction mechanism. Therefore, the kinetics, thermodynamics, reaction mechanism and thermal hazards identified under one heating rate could represent the characteristics of samples in general. To obtain more reliable results, the analysis and calculation in the following content will be carried out based on the data obtained by a 0.2 °C min⁻¹ heating rate.

The changes of heat generation by per mass sample versus temperature are shown in Fig. 2. Adding NA and SA greatly reduced the onset temperature for thermal decomposition and narrowed the temperature region (or time region) for decomposition reactions. However, two acids had different effects on the heat generation. The heat generation by pure NC was close to 4000 J g⁻¹. After adding NA, the heat generation was lower than 2000 J g⁻¹, reduced by 30% when comparing with pure NC. While add of SA improved the heat generation to outnumber 4000 J g⁻¹, higher than the value of pure NC.

Fig. 2. Comparison of per mass heat generation of three samples under a 0.2 °C min⁻¹ heating rate.

In summary, impurity of NA and SA both reduce the thermal stability of NC, and lead to a more dramatic exothermic behavior within shorter time region. The influences of two acids on thermal stability of NC could be concluded as follows. In perspective of onset temperature, the thermal stability order of three samples is, pure NC > NC with NA impurity > NC with SA impurity. According to maximum heat flow, the order is NC with SA impurity > NC with NA impurity > NC. For the dramatic extent of reaction (expressed by temperature region of exothermic reaction), the order is NC > NC with NA impurity > NC with SA impurity. And for the heat of reaction, the order is NC with SA impurity > NC > NC with NA impurity.

3.2 Autocatalytic mechanism analysis

Two methods are applied in this study to explore the autocatalytic reaction mechanism of these samples. The first method is to analyze the reaction profile. Reaction profile could to some extent indicate the autocatalytic mechanism. The relation between heat generation and temperature reflects the conversion rate of sample during reaction, and thus indicates possible mechanism by the reaction profile [12]. From Fig. 2, despite the differences in onset temperature and heat generation, there is a

similar pattern in changes of conversion rate over temperature. A sigmoidal model is reflected in three samples, representing autocatalytic thermal decomposition mechanism. The typical characteristic of sigmoidal model is that the initial and final stage demonstrate accelerating and decelerating behavior respectively, and the maximum reaction rate is achieved at a specific conversion rate during decomposition [12].

As Fig. 2 is obtained by heating samples under a constant rate, the reaction rate could change and influence reaction profiles. Therefore, three isothermal experiments were operated to prove the autocatalytic mechanisms. Isothermal heating method is a reliable way to detect and describe autocatalytic reaction. When the heat flow plot is in a shape of bell curve during isothermal condition, thermal decomposition of the chemical is an autocatalytic process [13, 14]. In this study, the temperatures were set close to the onset temperature of Peak 2 and Peak 1' for NC mixed with NA and 3, respectively. This is because these two peaks played major role in the entire exothermic process. Heat flow plots of three experiments are shown in Fig. 3.

Consistent with the reaction profile in Fig. 2, isothermal experiments also proved the autocatalytic reaction mechanism based on the bell curve. The reaction heats calculated from isothermal experiments are given in Table 5. The values of NC and 3 were close to the reaction heat obtained by constant heating experiments, indicating that the thermal decomposition process nearly completed during isothermal heating process. For NC mixed with NA, the reaction heat in isothermal experiment covered 70.80% of total heat during constant heating condition, indicating that Peak 1 in NC mixed with NA could generate over 29% of the heat and the reaction heat of Peak 2' in NC mixed with SA could be ignored. Moreover, Fig. 3 also indicated the obvious differences in thermal stability of three samples. Although they all followed autocatalysis mechanism, NC mixed with SA had the sharpest reaction curve with highest heat flow among three samples. The curves of NC and 2 were in a nearly symmetrical bell shape. But NC mixed with SA had a very sharp Peak 1 after started to release heat. It also took longest time for NC to reach exothermic peak. It is assumed that, adding acids changed the thermal decomposition process of NC by activating

intermediate products generated from NC decomposition. And this activation occurred before NC reached the maximum decomposition rate.

Fig. 3. Isothermal experimental results of three samples.

Table 5. Comparison of reaction heat in isothermal and constant heating experiments for three samples under a 0.2 min⁻¹ heating rate.

No.	ΔH_{iso} (J g ⁻¹)	ΔH (J g ⁻¹)	Proportions (%)
NC	3857.95	3865.065	99.81%
NC-NA	2212.89	3125.763	70.80%
NC-SA	3904.29	4058.088	96.21%

3.3 Calculation of kinetics and thermodynamics

To solve the kinetics and thermodynamics, the Arrhenius law is assumed. Model free kinetics under various heating rates is an advanced principle to solve the parameters. Based on the fundamental thermal decomposition function of $d\alpha/dt=k(T)f(\alpha)$, model free methods could obtain activation energy without assumption of reaction model, and thus avoid errors caused by selecting wrong model. A typical model free method, Kissinger method, was applied in this study. A first-order kinetics was assumed to calculate the pre-exponential factor. Kissinger method assumed that the maximum heat

flow characterizes the maximum reaction rate [15]. The basic function is Eq. (1),

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \quad (1)$$

where β represents heating rate and T_m could be obtained from heat flow plot in Fig. 1, 2 and 3. By plotting $\ln(\beta T_m^2)$ versus $1/T_m$ under three heating rates and making a linear fitting, E was derived by the slope. Logarithm of A was calculated from the expression given in ASTM E698 [16],

$$A = \beta \left(\frac{E}{RT_m^2}\right) \exp\left(\frac{E}{RT_m}\right) \quad (2)$$

To test the value, Ozawa method was used to determine E . Ozawa method can determine the activation energy of reactants without a precise knowledge of reaction mechanism, by using Eq. (6)[3]

$$\log\beta + 0.496\left(\frac{E}{RT_m}\right) = \text{Constant} \quad (3)$$

Similarly, plot $\log\beta$ against $1/T_m$ and make a linear fitting, E can be derived from the slope of straight line.

Table 6~7 list the results of E and A for all samples calculated by Kissinger and Ozawa method. Fig. 4~6 presents the curve fitting results by two kinetic methods. The activation energy calculated by Kissinger method is relatively lower than that by Ozawa method. But both methods indicated that adding acids reduced the activation energy of NC. Lowest activation energy was calculated for the Peak 2' of NC mixed with SA, which was 58.57 kJ mol⁻¹ by Kissinger method and 57.49 kJ mol⁻¹ by Ozawa method. The second lowest activation energy belongs to the Peak 1 in NC mixed with NA, which was 76.23 kJ mol⁻¹ by Kissinger method and 72.27 kJ mol⁻¹ by Ozawa method. This was nearly a half lower than Peak 1' of NC mixed with SA. This indicates that NC contaminated by NA has the lowest thermal stability and requires least energy to activate decomposition process. Therefore, the thermal stability order of three samples in perspective of activation energy, NC > NC with SA impurity > NC with NA impurity.

After obtaining the kinetic parameters, thermodynamic parameters of activation reaction, including free energy (ΔG^*), enthalpy (ΔH^*) and entropy (ΔS^*) can be derived by the Eq. (4)-(7) [14],

$$A \exp \frac{-E}{RT} = \nu \exp \frac{-\Delta G^*}{RT} \quad (4)$$

$$\Delta H^* = E - RT \quad (5)$$

$$\Delta G^* = \Delta H^* - T \Delta S^* \quad (6)$$

$$\nu = \frac{K_B T}{h} \quad (7)$$

where K_B and h are Boltzmann and Planck constant, respectively.

The thermodynamic values for all samples were calculated at peak temperature from heat flow plots by C80. Results based on the kinetics are given in Table 6 and 7. For all the peaks, the ΔG^* were close, ranging from 105.35 kJ mol⁻¹ to 127.50 kJ mol⁻¹. The pattern of ΔH^* values was consistent with the activation energy among all samples, with value of 55.11/54.03 kJ mol⁻¹ for Peak 2' of NC mixed with SA and 73.13/68.71 kJ mol⁻¹ for Peak 1 of NC mixed with NA. These values were much lower than other peaks. For NC by Ozawa method, Peak 1 and Peak 2', negative value of ΔS^* was derived.

Table 6. Kinetics and thermodynamics of NC under a 0.2 min⁻¹ heating rate.

Method	Kinetics			Thermodynamics		
	E	A	R^2	ΔG^*	ΔH^*	ΔS^*
	(kJ mol ⁻¹)	(s ⁻¹)		(kJ mol ⁻¹)	(Kj mol ⁻¹)	(J mol ⁻¹)
Kissinger	123.67	1.68×10 ¹⁴	0.934	113.60	120.30	16.56
Ozawa	114.24	9.41×10 ¹²	0.985	104.17	110.88	16.56

Table 7. Kinetics and thermodynamics of NC mixed with NA or SA under a 0.2 min⁻¹ heating rate for Peak 1.

Sample No.	Method	Kinetics			Thermodynamics		
		E	A	R^2	ΔG^*	ΔH^*	ΔS^*
		(kJ mol ⁻¹)	(s ⁻¹)		(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J mol ⁻¹)
NC-NA	Kissinger	76.23	6.42×10 ⁸	0.859	105.35	73.13	-86.46
	Ozawa	72.27	1.69×10 ⁸	0.879	110.93	68.71	-98.69
NC-SA	Kissinger	127.65	6.72×10 ¹⁴	0.956	112.96	124.30	28.14
	Ozawa	117.7	3.18×10 ¹³	0.962	113.23	114.35	2.77

237 **Table 8. Kinetics and thermodynamics of NC mixed with NA or SA under a 0.2**
 238 **min⁻¹ heating rate for Peak 2.**

Sample No.	Method	Kinetics			Thermodynamics		
		<i>E</i>	<i>A</i>	<i>R</i> ²	ΔG^*	ΔH^*	ΔS^*
		(kJ mol ⁻¹)	(s ⁻¹)		(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J mol ⁻¹)
NC-NA	Kissinger	138.67	1.57×10 ¹⁵	0.993	120.28	135.11	34.66
	Ozawa	127.71	6.62×10 ¹³	0.993	120.57	124.15	8.36
NC-SA	Kissinger	58.57	1.85×10 ⁵	0.653	119.63	55.11	-155.14
	Ozawa	57.49	1.33×10 ⁵	0.715	119.69	54.03	-157.90

239 **Fig. 4. Kinetics fitting results of NC by Kissinger method and Ozawa method.**
 240

Fig. 5. Kinetics fitting results of NC mixed with NA by Kissinger method and Ozawa method.

Fig. 6. Kinetics fitting results of NC mixed with SA by Kissinger method and Ozawa method.

3.4 Mechanism and hazards

Based on previous literatures [6, 7, 17], decomposition of NC starts by breaking –O-NO₂ bond and generates oxygen free radicals, CH₂O and NO₂ [18]. Oxygen free radicals turn into carbonyls by transferring its electrons into carbon atom. The -O-NO₂ bond scission is a continuous process and NO₂ plays role as activation of autocatalysis reaction [19]. The –C-O-C- bonds in glucopyranosyl ring also break, and CH₂O reacts with NO₂ at the same time. Ultimately, various gases such as CO_x and NO_x are generated, see Eq. (8) and (9). Given that acids were present in NC mixed with NA and 3, acid hydrolysis was responsible for the lower stability to start the decomposition process by function of [H⁺]. From the study of Brill and Gongwer [20], a chemical equilibrium between [H⁺] and RONO₂ occurred and generated intermediate products [RONO₂H⁺]. The secondary products liberated small amount of NO_x and increase the reaction rate. The form of [RONO₂H⁺] due to acid hydrolysis changed the reaction

process when temperature was lower than 200 °C, and promoted autocatalysis reactions. This principle could explain the promotion of decomposing process by two inorganic acids (see Eq. (10) and (11)).

Despite that all the samples showed autocatalytic characteristics, NA and SA have different effects on thermal decomposition of NC due to their chemical natures. There are two possible reasons. Firstly, the NA and SA had the same mass fraction, indicating that content of $[H^+]$ in SA was twice more than that of NA. Secondly, the differences in thermal behavior of SA and NA itself may account for it. NA could easily decompose under heating condition [9], so the first peak in NC mixed with NA may be caused by the instability of NA itself. The process generated NO_x , especially NO_2 , which acted as catalysis to promote the thermal decomposition process. While for SA, the $[H^+]$ played major role, so the first peak contributed to most of the reaction heat. However, this is a rough analysis for such a complex decomposition process. Additional experimental techniques are still required in future study to obtain a deeper understanding of possible mechanism and reaction kinetics.

Comparing with NC in high nitrogen content and applied for explosives, the sample in this study is relatively safer and commonly applied in chemical industry. However, the experiments by C80 identified that, not only does NC itself has high possibility to occur autocatalytic decomposition, contamination by NA and SA could greatly reduce its thermal stability by reducing onset temperature and generate large amount of heat in a very short time region. Particularly, SA could dramatically increase thermal hazards of NC once the decomposing starts. Therefore, much attention should be paid to during manufacturing, storage, processing, and transportation of NC.

4. Conclusions

The thermal decomposition characteristics and heat generation of pure NC, and its

mixture with NA and SA were researched using a C80 calorimeter. Two temperature models, constant heating under 0.2, 0.4 and 0.5 °C min⁻¹ heating rate and isothermal heating were applied. Characteristics of heat flow plots in various heating rate were analyzed. The autocatalytic mechanism was identified by reaction curve analysis and isothermal experiments. Kinetics and thermodynamics were obtained by two model free kinetic methods. The effect of acids on thermal decomposition of NC were analyzed. Major conclusions were obtained as follows.

(1) Both contamination of NA and SA promoted the thermal decomposition process of NC, reduced the onset temperature, and shorten the temperature region. SA had more significant influence on thermal decomposition of NC than NA in perspective of maximum heat flow, heat generation and temperature region. Mixture of NC with NA has the lowest initial temperature value of 62.53 °C.

(2) The catalytic mechanism was proved by both reaction curve analysis and isothermal experiment methods. Bell-shape curves were identified in all samples. The decomposition of pure NC and NC contaminated by two acids followed autocatalytic mechanism and generated large amount of heat. For pure NC and NC contaminated by SA, the heat generation during isothermal stage was very close to constant heating condition. Decomposition almost finished during isothermal heating condition.

(3) Kissinger method and Ozawa method were applied to calculated kinetics of pure NC and its mixture with two acids. Thermodynamic parameters were derived based on peak temperature of heat flow. Activation energy value by Ozawa method was smaller than Kissinger method. But two methods reflected the consistent results that, adding acids reduced the activation energy, and NC contaminated by NA had the lowest activation energy value to start thermal decomposition, which was 76.23 °C by Kissinger method and 72.27 °C by Ozawa method.

(4) The chemical equilibrium between [H⁺] and RONO₂ generated intermediate products [RONO₂H⁺], which decomposed into small amount of NO_x and increased the reaction rate. The mechanism for NA and SA to influence NC's decomposition was different. The differences in thermal decomposition of pure NA and SA itself accounted for such different effects.

321 Nomenclature and Units

A	pre-exponential factor (s^{-1})
ARC	accelerating rate calorimeter
C80	C80 micro calorimeter
E	activation energy ($J\ mol^{-1}$)
ΔG^*	free energy ($kJ\ mol^{-1}$)
h	plank constant
ΔH^*	free enthalpy ($kJ\ mol^{-1}$)
ΔH	reaction heat ($J\ g^{-1}$)
ΔH_{iso}	reaction heat for isothermal experiment ($J\ g^{-1}$)
H_m	peak heat flow ($mW\ g^{-1}$)
K_B	boltzmann constant
NC	nitrocellulose
ΔS^*	free entropy ($J\ mol^{-1}\ K^{-1}$)
T_{on}	onset temperature ($^{\circ}C$)
T_m	peak temperature ($^{\circ}C$)
ΔT	reaction temperature region ($^{\circ}C$)
ΔT_m	Reaction temperature region to reach T_m ($^{\circ}C$)

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382