The exothermal decomposition of nitrocellulose in mixed acids

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The exothermic decomposition of nitrocellulose in a solution of mixed acid was studied in order to determine the conditions for safe production of nitrocellulose by means of the nitration of cellulose with mixtures of nitric acid and sulphuric acid. Isothermal decomposition tests were carried out and a temperature slightly higher than the nitration temperature in manufacturing was adopted as an experimental condition. The results obtained are as follows.

Nitrocellulose in mixed acid underwent exothermic degradation after a long induction period, which was affected by the reaction temperature. This degradation showed the maximum rate in the middle of the reaction, which indicated the reaction to be autocatalytic. The activation energies obtained by Arrhenius plots of rate constants from the autocatalytic rate equation were 31.4 ～59.1 kJ/mol. Moreover, plots of the logarithm of the induction period t vs. the inverse of reaction temperature also showed good linearity according to the Arrhenius- type equation, and the obtained activation enrgies were 37.3～60.4 kJ/mol.

The induction period after which the exothermic reaction commenced decreased with the increasing NC / mixed acids ratio. An increase in the content of nitric acid in the mixed acid then had a decreasing effect on the induction period. Moreover, this degradation was affected by atmospheric gases, and nitrogen dioxide accelerated the reaction.

1. Introduction

Nitrocellulose (NC, Nitrocotton) is one of the most reactive chemicals. Because of this reactive nature, enormous fires and incidental explosions have been reported in its manufacturing. Moreover, aging of nitrocellulose under long term storage causes a change in the practical performance or an incidental explosion. Extensive data on the aging of explosives have been accumulated from the viewpoint of safety in manufacturing, storage, and use or operational reliability[1),2),3)]. However, few kinetic data are available on nitrocellulose decomposition in mixed acid which are required for safe production.

In this paper, the thermal behavior of nitrocellulose in a solution of mixed acid was studied in order to determine the conditions for safe production of nitrocellulose by means of the nitration of cellulose with mixtures of nitric acid and sulphuric acid. As an experimental method, isothermal decomposition experiments were carried out at temperatures ranging from 50～75 ℃ which are slightly higher than the nitration temperature in practical manufacturing. Based on the consideration of the effect of temperature, NC/acid ratio, and acid composition on NC decomposition in the mixed acid, the thermal decomposition behavior and mechanisms of nitrocellulose in mixed acid were investigated to understand the thermal behavior of nitration during the practical nitration process in order to determine the conditions for safe production.

2. Experimental

2. 1 Materials

Four types of industrial grade NC samples used in these experiments were supplied by Asahi Chemi-

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cal Industry Co., Ltd. LB type NC is in powdered form and its nitrogen content is 11.6 %. LA type NC is in a cotton flake form having a nitrogen content of 11.8 %. HB type NC is in a powdered form having an 11.8% nitrogen content. HA type NC is in a cotton flake form having a 12.1% nitrogen content.

Mixed acids have the compositions of nitric acid (HNO_3)/ sulphuric acid (H_2SO_4)/ water(H_2O) = 60/20/20, 50/30/20, 40/40/20, 30/50/20 and 20/60/20 by weight. Thermal analyses were carried out for samples of the mixtures with 960 parts of mixed acid and 4 parts of NC, 480/4, 240/4, 96/4 and 48/4.

2. 2 Thermal analysis

Thermal analysis was performed using a handmade microcalorimetric apparatus under argon gas atmosphere, in which the heating rate was 2 K/min and the sample weight was 900 mg (36 mg of NC and 864 mg of mixed acid). Preliminary experiments showed that the temperature rise in the sample solution of mixed acid and NC caused by exothermic decomposition was within 1K.

Exothermic properties in the isothermal decomposition of NC were examined using the handmade microcalorimetric apparatus under atmospheres of argon gas, air, and argon with about 1 vol% nitrogen dioxide. Isothermal operation of thermal analyses for NC in mixed acid was carried out at temperatures ranging from 50~75 ℃.

3. Results

3. 1 Thermal decomposition of nitrocellulose in mixed acid

Fig.1 shows an example of the DTA curves for NC (4 wt%, LB type NC) in mixed acid(96 wt%, HNO_3/H_2SO_4/H_2O=60/20/20 by weight) under argon. NC began to undergo exothermic decomposition in the mixed acid at a temperature of 65 ℃, evolving nitrogen dioxide gas. This exothermic reaction ceased at the temperature of about 90 ℃, producing a brownish yellow solution. The decomposition temperatures do not differ with the types of NC. Pure nitrocellulose decomposed thermally at temperatures ranging from 180 ~ 250 ℃ in argon. Thus, the NC decomposition in mixed acid occurred at a lower temperature compared with pure NC.

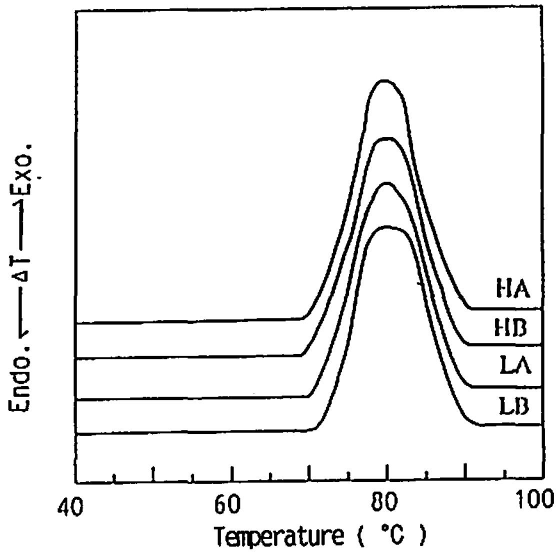

Fig. 1 An example of DTA curves of NC in mixed acid

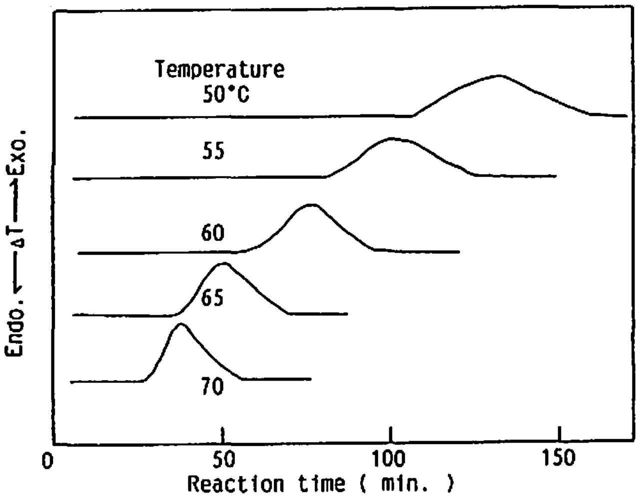

Fig. 2 Isothermal decomposition of NC (36 mg) in mixed acid (864 mg, H_2SO_4/ HNO_3/ water=60/20/20 by weight) obtained by micro-calorimetry

3. 2 Isothermal decomposition of nitrocellulose in mixed acid

Under isothermal condition, NC underwent exothermic decomposition in mixed acid at temperatures ranging from 50~75 ℃ within 400 minutes. Fig.2 shows the results of isothermal decomposition of NC(36 mg, LB type NC) in mixed acid(864 mg, H_2SO_4/HNO_3/water = 60/20/20 by weight)under argon obtained by microcalorimetry. There are two

Table 1 Induction period and kinetic parameters at various temperatures for the thermal decomposition of NC in mixed acid under argon

Temp. (℃)	Rate constant k (min.-1)	Induction time (min.)
40	0. 009	414
50	0. 018	184
60	0. 039	100
70	0. 060	55

Mixed acid : NC(LB type NC) ; 96 : 4 (by weight), Mixed acid; HNO_3 / H_2SO_4 / H_2O = 60/20/20 by weight.)

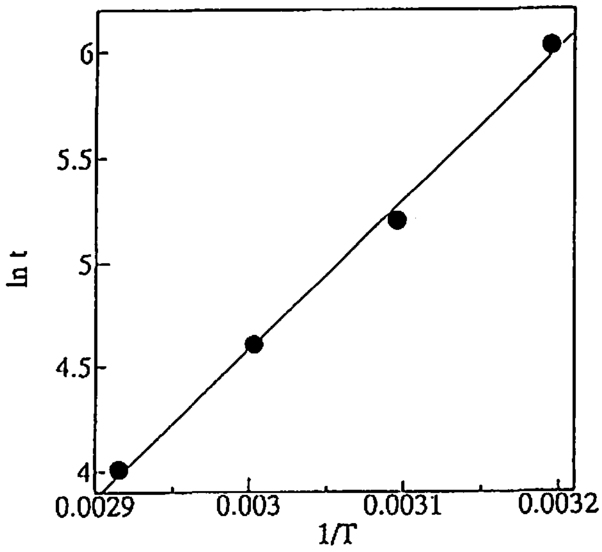

Fig. 3 ln t vs. 1/T plot with regard to Fig.2

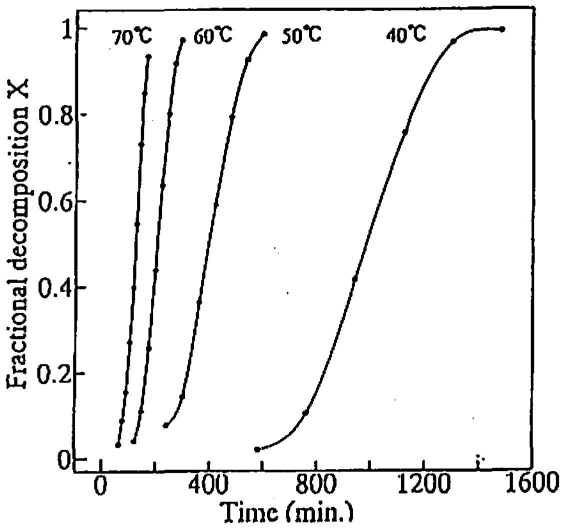

Fig. 4 Fractional decomposition (x) vs. time curves obtained from Fig.2

characteristic features of NC decomposition in mixed acid. One is that the NC exothermic decomposition had an autocatalytic nature. The other is that the NC decomposition had an induction period.

Many researchers reported that the thermal decomposition reaction of pure nitrocellulose is autocatalytic. However, the mechanisms of the thermal decomposition of pure nitrocellulose and that in mixed acid may not be same.

The induction period is a very important factor for safe handling in NC production. Table 1 shows the induction period for the thermal decomposition of NC (4 wt%, LB type NC) in mixed acid(96 wt%, $HNO_3/H_2SO_4/H_2O$= 60/20/20 by weight) at various temperatures under argon. Based on this thermal analysis, the induction period decreased with increasing reaction temperature. Plots of the logarithm of the induction period t (min) vs. the inverse of reaction temperature showed good linearity according to the following Arrhenius-type equation (1):

$$\ln t = Ea/RT + \mathrm{la}\, A \qquad (1)$$

where t is the induction period, Ea the temperature dependence for the initiation of the exothermic reaction (activation energy for initiation) and A a constant. Fig.3 is the ln t vs. 1/T plot with regard to Fig.2, and shows good linearity. Ea obtained from the decline in this Arrhenius-type plot was 59 kJ/mol. As stated below, the induction period decreased with an increase in the NC/mixed acid ratio or an increase in the concentration of nitric acid in the mixed acid.

3. 3 Kinetic study of the decomposition of nitrocellulose in mixed acid

Once the decomposition is initiated, the rate increased with the reaction time and reached a maximum in the middle of the exothermic reaction. This exothermic reaction rate increased with an increase of NC / mixed acid ratio or an increase in the concentration of nitric acid in the mixed acid. Fractional decomposition (x) at time t is defined as the ratio of the peak area up to the time t to the total area at the end of the reaction. Fractional decomposition (x) vs. time curves(Fig.4) obtained from Fig.2 have an s-shape. It is known that an S-shape for a fractional decomposition vs. reaction time curve

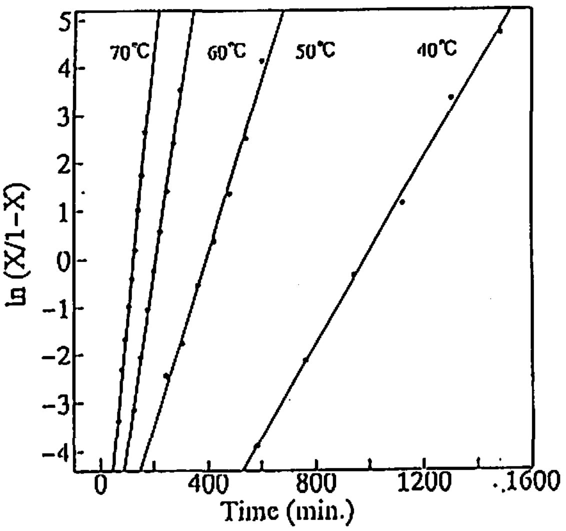

Fig. 5 Applicability of the results of Fig.3 to the autocatalytic rate equation (2)

often represents an autocatalytic reaction. Fig.5 shows the applicability of the results of Fig.4 to the autocatalytic rate equation (2):

$$\ln(x/(1-x)) = kt \qquad (2)$$

where x is the fractional decomposition of nitrocellulose calculated from the thermogram in Fig.2, k the rate constant for the autocatalytic decomposition and t the reaction time. This plot shows good linearity, and the obtained rate constants are shown in Table 1. Arrhenius plots of the rate constants k obtained from Fig.4 gave an activation energy of 57 kJ/mol.

Many NC decomposition studies indicate that the decomposition of pure dry NC follows the autocatalytic rate equation[2] due to the catalytic nature of the product nitrogen oxides. Our NC decomposition experiments in mixed acid also follows the same rate equation but with a longer induction period. The activation energy of the dry decomposition also differs from that in the mixed acid, and those values were reported to be 180~200 kJ/mol[3]. Thus, it can be deduced that the decomposition mechanisms of NC in the dry condition and in the mixed acd are different.

3. 4 Effect of some factors on the decomposition of nitrocellulose in mixed acid

In order to consider the effect of compositions of mixed acid, isothermal experiments were carried out for the mixed acid which consisted of nitric acid (HNO_3)/sulphuric acid (H_2SO_4)/ water(H_2O) = 60/20/20, 50/30/20, 40/40/20, 30/50/20 and 20/60/20 by weight, respectively. Every composition had an induction period, and fractional decomposition vs. time curves showed a sigmoidal shape. Table 2 shows the induction periods and kinetic parameters for various acid compositions. As stated before, the induction period decreased with an increase in the NC / mixed acid ratio or with an increase in the concentration of nitric acid in the mixed acid. Regarding the rate constants, the same results were obtained with respect to the induction time. That is, the rate constant k for the autocatalytic decomposition increased with an increase in the NC / mixed acid ratio or with an increase in the concentration of nitric acid in the mixed acid.

Fractional decomposition (x) vs. time curves obtained from the isothermal decomposition of NC in

Table 2 Kinetic parameters for the decomposition of NC in mixed acid for various acid compositions

N:S:W (by wt.)		Rate constant (Induction time) k (min.)				Ea (Induction time) (kJ/mol)
	Temp. ℃	40	50	60	70	
60:20:20		0.039(187)	0.063(96)	0.105(72)	0.162(36)	43.1(46.7)
50:30:20		0.023(240)	0.044(129)	0.077(82)	0.132(43)	48.0(50.1)
40:40:20		0.018(294)	0.035(144)	0.057(89)	0.101(48)	51.3(52.9)
30:50:20		0.012(352)	0.022(159)	0.040(96)	0.075(53)	55.2(55.3)
20:60:20		0.008(458)	0.017(244)	0.036(117)	0.058(59)	59.1(60.4)

N; Nitric acid, S; Sulfuric acid, W; Water, Ea in brackets; Calculated values from induction time, Mixed acid : NC (LB type NC);96:4 (by weight)

Table 3 Kinetic parameters for the isothermal decomposition of nitrocellulose in the argon-NO_2 atmosphere

Temp. (℃)	Rate constant k (min.$^{-1}$)	Induction time (min.)
30	0.472	0
40	0.679	0
50	1.232	0

Acid (mixed acid), Sulfuric acid: Nitric acid: Water = 60:20:18 by weight, Mixed acid: NC (LB type NC); 96:4 (by weight)

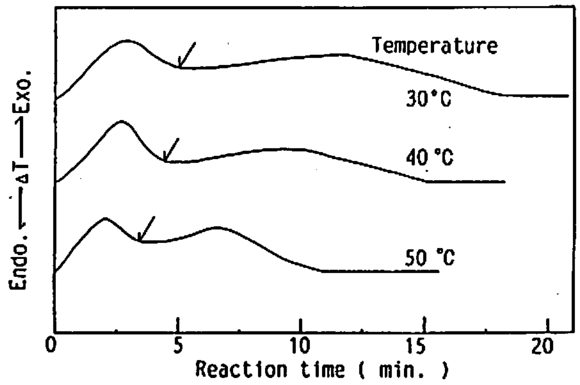

Fig. 6 Isothermal decomposition of nitrocellulose under argon-NO_2 atmosphere (NO₂ flow has been stopped at the time indicated by the arrows, and argon flow has been started thereafter.)

the mixed acid in the argon−NO_2 atmosphere also had an s- shape. Rate constants for the NO_2-catalyzed NC decomposition are shown in Table 3. Arrhenius plots of this rate constant k gave a very low activation energy of 30.4 kJ/mol. However, the isothermal decomposition of nitrocellulose in the argon-NO_2 atmosphere showed the following characteristic features compared with the experiment without NO_2. One is that NC decomposes immediately without any induction period. This tells us that NO_2 accelerates the initial reaction of the decomposition. Another is that the NC decomposition is never completed in the NO_2 containing atmosphere in spite of the accelerating effect of NO_2. This tells us that NO_2 accelerates the NC decomposition, but that the decomposition stops on the way, showing a kind of equilibrium between the reaction species and NO_2. Fig.6 shows the experimental evidence of the catalytic action of NO_2 on NC decomposition, in which the isothermal decomposition was carried out under argon-NO_2 flow until the time when the decomposition stopped(this time is indicated by the arrows in Fig.6), and thereafter only argon was kept flowing. In this experiment, though a kind of equilibrium was once attained under argon-NO_2 flow, the exothermic reaction again occurred in argon.

Table 4 shows the effect of acid amount on the exothermal decomposition of NC in mixed acid. The induction period decreased with the increasing NC/mixed acid ratio. Table 5 shows the effect of the type of NC on the exothermal decomposition of NC in mixed acid. Induction periods were different with different kinds of NC, but the activation energies obtained from the induction periods and the kinetic parameters have the same value regardless of the

Table 4 Effect of acid amount on the exothermal decomposition of NC in mixed acid

Acid:NC (by wt.)		Induction time (min.)			Ea (kJ/mol)
	Temp. ℃	50	60	70	
48:4		57	33	16	57.1(58.4)
96:4		181	100	55	57.0(59.4)
240:4		2080	1235	590	58.4(57.9)
480:4		7152	3937	2016	57.0(58.3)
960:4		10059	5086	2912	56.9(57.1)

Acid (mixed acid), Sulfuric acid: Nitric acid: Water = 60:20:18 by weight, Ea in brackets; Calculated Ea from induction period, NC; LB type NC

Table 5 Effect of type of NC on the exothermal decomposition of NC in mixed acid

Type of NC		Induction time (min.)				Ea (kJ/mol)
	Temp. ℃	40	50	60	70	
LB			181	100	55	57.0(59.4)
HB		211	124	76	50	39.7(43.0)
HA			54	36	24	31.4(37.3)
LA		530	312	176	120	41.9(44.9)

Acid (mixed acid), Sulfuric acid: Nitric acid: Water = 60:20:18 by weight, Mixed acid: NC (LB type NC); 96:4 (by weight), Ea in brackets; Calculated Ea from induction period

type of NC.

4. Conclusions

Nitrocellulose in mixed acid underwent autocatalytic degradation after a long induction period, which was affected by the reaction temperature. The activation energy obtained from the autocatalytic rate equation was about 31.4～59.1 kJ/mol. Moreover, the induction period decreased with an increasing NC/ mixed acid ratio. An increase in the content of nitric acid in the mixed acid had a decreasing effect on the induction period. Plots of the logarithm of the induction period t vs. the inverse of the reaction temperature showed good linearity according to the Arrhenius-type equation, and the obtained Ea was about 37.3～60.4 kJ/mol.

Nitrocellulose in the mixed acid underwent autocatalytic degradation after a long induction period, which was affected by the reaction temperature, the amount of acid, and its composition. Moreover, nitrogen dioxide shortened this induction period and accelerated the reaction.

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混酸中でのニトロセルロースの発熱分解

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硝酸と硫酸からなる混酸中でのニトロセルロースの発熱分解を，自製の熱分析装置を用いて，実際の硝化温度よりも若干高い温度で検討した。得られた結果は以下の通りである。

混酸中のニトロセルロースは誘導期間の後に発熱分解を起こし，この誘導期間や発熱分解反応の速度は反応温度によって変化した。等温反応では発熱分解反応は反応の中間に最大速度を示す，自触媒型に特有の反応率一時間曲線を示した。この反応の活性化エネルギーは31.4～59.1kJ/molであった。誘導期から求めた活性化エネルギーは37.3～60.4kJ/molであった。

発熱反応が開始する誘導期は，混酸量の影響を受けてニトロセルロース量が増加するにつれ，また，混酸中の硝酸量が増加するにつれて減少した。さらに，分解に及ぼす雰囲気ガスの影響も認められ，二酸化窒素は反応を加速した。

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