

Kinetics of the First Order Autocatalytic Decomposition Reaction of Nitrocellulose (13.86% N)

GUO, Peng-Jiang^a(郭鹏江) HU, Rong-Zu^{*a,b}(胡荣祖) NING, Bin-Ke^b(宁斌科)
 YANG, Zheng-Quan^b(杨正权) SONG, Ji-Rong^a(宋纪蓉) SHI, Qi-Zhen^a(史启祯)
 LU, Gui-E^c(路桂娥) JIANG, Jin-You^c(江劲勇)

^a Shaanxi Key Laboratory of Physico-Inorganic Chemistry, Department of Chemistry, Northwest University, Xi'an 710069, China

^b Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi 710065, China

^c Ordnance Engineering Institute, Shijiazhuang, Hebei 05000, China

The kinetics of the first order autocatalytic decomposition reaction of nitrocellulose (NC, 13.86% N) was studied by using DSC. The results show that the DSC curve for the initial 50% of conversion degree of NC can be described by the first order autocatalytic equation

$$\frac{dy}{dt} = -10^{16.3} \exp\left(-\frac{181860}{RT}\right) y - 10^{16.7} \exp\left(-\frac{173050}{RT}\right) y(1-y)$$

and that for the latter 50% conversion degree of NC described by the reaction equations

$$\frac{dy}{dt} = -10^{16.4} \exp\left(-\frac{154820}{RT}\right) y \quad (n=1) \quad \text{and} \quad \frac{dy}{dt} = -10^{16.9} \exp\left(-\frac{155270}{RT}\right) y^{2.80} \quad (n \neq 1).$$

Keywords first order autocatalytic reaction, NC, kinetics, DSC

Introduction

Much attention has been paid to nitrocellulose containing 13.86% of nitrogen as an ingredient of propellants. The kinetics of the first order autocatalytic decomposition reaction of nitrocellulose (NC) containing 12.60%—13.42% of nitrogen has been reported,¹⁻³ but the kinetics of the first order autocatalytic decomposition reaction for NC (13.86% N) has not been studied. In this work, we studied the kinetics of thermal decomposition processes of NC (13.86% N).

Experimental

Materials

The nitrocellulose containing 13.86% of nitrogen used in this work was prepared and purified according to Ref. 4.

Experimental

In the present experiments, the initial data needed for calculating all the kinetic parameters were obtained using a CDR-1 differential scanning calorimeter (Shanghai Tianping Instrument Factory, China) with an aluminum cell. The conditions of the DSC analyses were: sample mass, about 0.7 mg; heating rate, 18 K · min⁻¹,

respectively; calorimetric sensitivities, ±20.92 mJ · s⁻¹; atmosphere, static air; reference sample, α-Al₂O₃; the precision of temperature was 0.25 K; the temperature and heat were calibrated using pure indium and tin powders. Heating rate β was calculated according to the actual rising rate of temperature from 50 °C to the temperature at the end of reaction.

Results and discussion

Solution of the first order autocatalytic equation for the thermal decomposition reaction of NC under non-isothermal conditions

The first order autocatalytic equation for the thermal decomposition of NC under isothermal conditions is

$$\frac{dy}{dt} = -k_1(T)y - k_2(T)y(1-y) \quad (1)$$

where y is the fraction of the unreacted reagents; T the temperature, K; t the time, s; $k_1(T)$ the rate constant of the first order reaction, s⁻¹; $k_2(T)$ the rate constant of the first order autocatalytic reaction involving the reaction products, s⁻¹, defined by

$$k_i(T) = A_i e^{E_i/RT}, \quad i = 1, 2 \quad (2)$$

* E-mail: hurongzu@public.xa.sn.cn

Received May 12, 2003; revised and accepted September 8, 2003.

Project supported by the Science and Technology Foundation of Shaanxi Key Laboratory of Physico-Inorganic Chemistry (No. 29-3, 2001), and the Science and Technology Foundation (No. 514550101) of Propellant and Explosive Combustion of China.

where A is the pre-exponential factor, s^{-1} ; E the activation energy, $J \cdot mol^{-1}$; R the gas constant, $8.314 J \cdot mol^{-1} \cdot K^{-1}$.

If the heating rate (β) under non-isothermal conditions is defined by

$$\beta = \frac{dT}{dt} \quad (3)$$

substituting the Eq. (3) into Eq. (1) gives

$$\beta \frac{dy}{dT} = -k_1(T)y - k_2(T)y(1-y) \quad (4)$$

$$\beta \frac{dy}{dT} = -[k_1(T)y - k_2(T)]y + k_2(T)y^2 \quad (5)$$

This is a Bernoulli's equation. In order to obtain the solution of Eq. (5), the variables in Eq. (5) can be separated to give

$$y^{-2} \frac{dy}{dT} = -\frac{k_1(T)+k_2(T)}{\beta} y^{-1} + \frac{k_2(T)}{\beta} \quad (6)$$

$$\frac{d(y^{-1})}{dT} = \frac{k_1(T)+k_2(T)}{\beta} y^{-1} - \frac{k_2(T)}{\beta} \quad (7)$$

By introducing the notation: $z = y^{-1}$, one obtains:

$$\frac{dz}{dT} = \frac{k_1(T)+k_2(T)}{\beta} z - \frac{k_2(T)}{\beta} \quad (8)$$

which is a first order linear equation and can be solved by the variation of parameter.

For the corresponding first order homogeneous linear equation

$$\frac{dz}{dT} = \frac{k_1(T)+k_2(T)}{\beta} z \quad (9)$$

separating its variables gives

$$\frac{dz}{z} = \left[\frac{k_1(T)}{\beta} + \frac{k_2(T)}{\beta} \right] dT \quad (10)$$

where $T: T_0 \rightarrow T$; $y: y_0 \rightarrow y$; $z: z_0 \rightarrow z$ and $y_0=1$, $z_0=1$.

Integration of Eq. (10) gives

$$\int_{z_0}^z \frac{dz}{z} = \int_{T_0}^T \left[\frac{k_1(T)}{\beta} + \frac{k_2(T)}{\beta} \right] dT \quad (11)$$

$$\ln \frac{z}{z_0} = \frac{A_1}{\beta} \int_{T_0}^T e^{-E_1/RT} dT + \frac{A_2}{\beta} \int_{T_0}^T e^{-E_2/RT} dT \quad (12)$$

Setting

$$S_1(T) = \int_{T_0}^T e^{-E_1/RT} dT \quad (13)$$

and

$$S_2(T) = \int_{T_0}^T e^{-E_2/RT} dT \quad (14)$$

where $S_1(T)$ and $S_2(T)$ are the integrals of the Arrhenius function, the Eq. (12) may be expressed as

$$\ln \frac{z}{z_0} = \frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T) \quad (15)$$

or

$$z = z_0 \exp \left[\frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T) \right] \quad (16)$$

Setting

$$z_0 = V(T) \quad (17)$$

Eq. (16) becomes

$$z = V(T) \cdot \exp \left[\frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T) \right] \quad (18)$$

$$\begin{aligned} \frac{dz}{dT} &= \frac{dV(T)}{dT} \cdot \exp \left[\frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T) \right] + \\ &V(T) \exp \left[\frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T) \right] \left[\frac{A_1}{\beta} S_1'(T) + \frac{A_2}{\beta} S_2'(T) \right] \end{aligned} \quad (19)$$

where

$$S_1'(T) = e^{-E_1/RT} \quad (20)$$

$$S_2'(T) = e^{-E_2/RT} \quad (21)$$

Substituting Eq. (19) into Eq. (8), we have

$$\frac{dV(T)}{dT} = -\frac{k_2(T)}{\beta} \exp \left\{ -\left[\frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T) \right] \right\} \quad (22)$$

Substituting $z=z_0=1$, $S_1(T_0)=0$ and $S_2(T_0)=0$ when $T=T_0$ into Eq. (18), we obtain

$$V(T_0) = 1 \quad (23)$$

Integrating Eq. (22), yields

$$\int_{V(T_0)}^{V(T)} dV(T) = -\frac{1}{\beta} \int_{T_0}^T k_2(T) \cdot \exp\left\{-\left[\frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T)\right]\right\} dT \quad (24)$$

and

$$V(T) = 1 - \frac{1}{\beta} \int_{T_0}^T k_2(T) \cdot \exp\left\{-\left[\frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T)\right]\right\} dT \quad (25)$$

Substituting Eq. (25) into Eq. (18), we obtain

$$z = \left(1 - \frac{1}{\beta} \int_{T_0}^T k_2(T) \cdot \exp\left\{-\left[\frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T)\right]\right\} dT\right) \times \exp\left[\frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T)\right] \quad (26)$$

Substituting the defined $z = y^{-1}$ into Eq. (26), we have

$$y(T) = \frac{\exp\left\{-\left[\frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T)\right]\right\}}{1 - \frac{1}{\beta} \int_{T_0}^T k_2(T) \cdot \exp\left\{-\left[\frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T)\right]\right\} dT} \quad (27)$$

This is the solution of the first order autocatalytic kinetic equation under non-isothermal conditions. Eq. (27) describes the temperature dependence of the concentration for the first order autocatalytic reaction before the inflection point in the DSC curve (for NC, the point corresponds to about 50% of conversion degree).

Solution of the kinetic equation for the thermal decomposition in the deceleration period under nonisothermal conditions

The rate equation for n th order for describing the deceleration period after the inflection point in the DSC curve (for NC, the point corresponds to the latter 50% of conversion degree) is

$$\frac{dy}{dt} = -k_3(T) y^n \quad (28)$$

where $k_3(T)$ is the rate constant of the decomposition reaction in the deceleration period defined by

$$k_3(T) = A_3 e^{-E_3/RT} \quad (29)$$

Inserting Eq. (3) into Eq. (28), we get

$$\beta \frac{dy}{dT} = -k_3(T) y^n \quad (30)$$

Integration Eq. (30) yields

$$\int_1^y y^{-n} dy = -\frac{A_3}{\beta} \int_{T_0}^T e^{-E_3/RT} dT \quad (31)$$

$$\frac{1}{1-n} y^{1-n} - \frac{1}{1-n} = -\frac{A_3}{\beta} \int_{T_0}^T e^{-E_3/RT} dT \quad (32)$$

Setting that

$$S_3(T) = \int_{T_0}^T e^{-E_3/RT} dT \quad (33)$$

and inserting Eq. (33) into Eq. (32), we have

$$\text{when } n \neq 1, y(T) = \left[1 + \frac{(n-1)A_3}{\beta} S_3(T)\right]^{\frac{1}{1-n}} \quad (34)$$

$$\text{when } n = 1, y(T) = \exp\left[-\frac{A_3}{\beta} S_3(T)\right] \quad (35)$$

Eqs. (34) and (35) are the solutions of the decomposition reaction kinetic equation in the deceleration period under non-isothermal conditions. They describe the temperature dependence of the concentration for the latter 50% of conversion degree in the DSC curve.

Numerical method for solving the first order autocatalytic kinetic equation and the simple kinetic equation

With respect to Eq. (27), functions $Q(T)$ and $W(T)$ are introduced and defined by Eqs. (36) and (37), respectively

$$Q(T) = \frac{A_1}{\beta} S_1(T) + \frac{A_2}{\beta} S_2(T) \quad (36)$$

$$W(T) = \frac{1}{\beta} \int_{T_0}^T k_2(T) e^{-Q(T)} dT = \frac{A_2}{\beta} \int_{T_0}^T \exp\left\{-\left[\frac{E_2}{RT} + Q(T)\right]\right\} dT \quad (37)$$

Inserting Eqs. (36) and (37) into Eq. (27), we obtain

$$y(T) = \frac{e^{-Q(T)}}{1 - W(T)} \quad (38)$$

The data from the DSC curve are $T_i, y_i; i=1, 2, \dots, N$, in which the initial 50% of conversion degree includes m points of data ($T_i, y_i; i=1, 2, \dots, m$), and the latter 50% of conversion degree includes ($N-m$) points of data ($T_i, y_i; i=m+1, \dots, N$). Inserting the initial m data into the function of sum of squares of deviation, we obtain

$$F_1(E_1, A_1, E_2, A_2) = \sum_{i=1}^m \left\{ y_i - \frac{e^{-Q(T_i)}}{1-W(T_i)} \right\}^2 \quad (39)$$

where

$$Q(T_i) = \frac{A_1}{\beta} S_1(T_i) + \frac{A_2}{\beta} S_2(T_i) = Q(T_{i-1}) + \frac{A_1}{\beta} \int_{T_{i-1}}^{T_i} e^{-E_1/RX} dX +$$

$$\frac{A_2}{\beta} \int_{T_{i-1}}^{T_i} e^{-E_2/RX} dX = Q(T_{i-1}) + \frac{A_1 EX1_i + A_2 EX2_i}{\beta} \quad (40)$$

where

$$EX1_i = \int_{T_{i-1}}^{T_i} e^{-E_1/RX} dX \quad (41)$$

$$EX2_i = \int_{T_{i-1}}^{T_i} e^{-E_2/RX} dX \quad (42)$$

$$W(T_i) = W(T_{i-1}) + \frac{A_2}{\beta} \int_{T_{i-1}}^{T_i} \exp \left\{ - \left[\frac{E_2}{RX} + Q(X) \right] \right\} dX =$$

$$W(T_{i-1}) + \frac{A_2}{\beta} WX_i \quad (43)$$

where

$$WX_i = \int_{T_{i-1}}^{T_i} \exp \left\{ - \left[\frac{E_2}{RX} + Q(X) \right] \right\} dX \quad (44)$$

We worked out programs by using Powell's optimization method⁵ to evaluate the minimum of the objective functions, in which the integrals EX1_{*i*}, EX2_{*i*}, and WX_{*i*} are calculated by using Gauss numerical integration method containing 16 nodes. The three-point quadratic parabola method⁶ is used in the one-dimension searching of the Powell's method.

The objective function of Eq. (34) is

$$F_3(E_3, A_3, n) = \sum_{i=1+m}^N \left\{ y_i - \left[1 + \frac{n-1}{\beta} A_3 S_3(T_i) \right]^{\frac{1}{1-n}} \right\}^2 \quad (45)$$

The objective function of Eq. (35) is

$$F_2(E_3, A_3) = \sum_{i=1+m}^N \left\{ y_i - \exp \left[- \frac{A_3}{\beta} S_3(T_i) \right] \right\}^2 \quad (46)$$

Similarly, the minimums of F_2 and F_3 are calculated by Powell's method.

Calculated results of the kinetic parameters of the autocatalytic reaction

The original data ($T_i, y_i; i=1, 2, \dots, 129$) used for the calculation of E_1, E_2, A_1, A_2, E_3 and A_3 including the data from the first part of the DSC curve ($T_i, y_i; i=1, 2, \dots, 50$) and those of the remaining part ($T_i, y_i; i=50, \dots, 129$) are taken from the DSC curve in Figure 1.

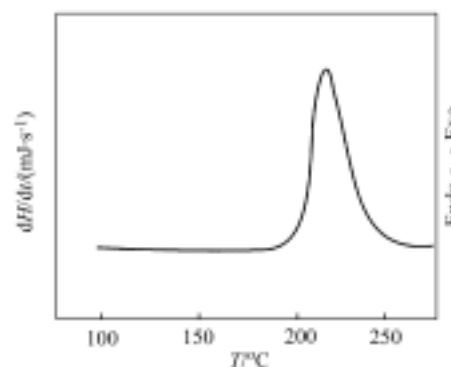


Figure 1 Typical DSC curve for NC (13.86% N) at a heating rate of 18 K · min⁻¹.

The kinetic parameters determined by fitting Eqs. (27), (34) and (35) to the experimental data by using Powell's optimization method are given in Table 1.

Conclusions

According to the above-mentioned results, we think that the DSC curve for the initial 50% of conversion degree of NC can be described by the first order autocatalytic equation

$$\frac{dy}{dt} = -10^{16.3} \exp \left(- \frac{181860}{RT} \right) y -$$

$$10^{16.7} \exp \left(- \frac{173050}{RT} \right) y(1-y)$$

Table 1 Results of analysis of the thermal decomposition data for NC (13.86% N) by Eqs. (27), (34) and (35)

<i>y</i>	Eq.	$E_1/(\text{kJ} \cdot \text{mol}^{-1})$	$E_2/(\text{kJ} \cdot \text{mol}^{-1})$	A_1/s^{-1}	A_2/s^{-1}	$E_3/(\text{kJ} \cdot \text{mol}^{-1})$	A_3/s^{-1}	<i>n</i>	SD ^a
1.00—0.50	(27) (<i>n</i> =1)	181.86	173.05	10 ^{16.3}	10 ^{16.7}				0.0433
	(35) (<i>n</i> =1)					154.82	10 ^{16.4}		0.0559
0.50—0.03	(34) (<i>n</i> ≠1)					155.27	10 ^{16.9}	2.80	0.0650

^a SD: standard deviation: 0.0433, 0.0559 and 0.0650 are the values of SD corresponding to functions F_1, F_2 and F_3 , respectively.

and that for the latter 50% conversion degree of NC described by the reaction equations

$$\frac{dy}{dt} = -10^{16.4} \exp\left(-\frac{154820}{RT}\right) y \quad (n=1)$$

and

$$\frac{dy}{dt} = -10^{16.9} \exp\left(-\frac{155270}{RT}\right) y^{2.80} \quad (n \neq 1)$$

References

- 1 Esenreich, N.; Pfeil, A. *Thermochim. Acta* **1983**, *61*, 13.
- 2 Eisenreich, N. *Ph.D. Dissertation*, Technical University of Munich, Munich, **1978**.
- 3 Jutier, J. J.; Harrison, Y.; Premont, S.; Prud'homme, R. E. *J. Appl. Poly. Sci.* **1987**, *33*, 1359.
- 4 Ning, B.-K. *Ph.D. Dissertation*, Zhejiang University, Hangzhou, **2003** (in Chinese).
- 5 Powell, M. J. D. *Comput. J.* **1964**, *7*, 155.
- 6 Phillips, G. M.; Taylor, P. J. *Theory and Applications of Numerical Analysis*, Academic Press, London and New York, **1973**, p. 50; p. 138.

(E0305124 LI, L. T.)