Journal of Thermal Analysis and Calorimetry, Vol. 58 (1999) 403-411

STUDIES ON THE KINETICS OF THE FIRST ORDER AUTOCATALYTIC DECOMPOSITION REACTION OF HIGHLY NITRATED NITROCELLULOSE

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Abstract

The kinetics of the first order autocatalytic decomposition reaction of highly nitrated nitrocellulose (HNNC, 14.14%N) was studied by using thermogravimetry (TG). The results show that the TG curve for the initial 50% of mass-loss of HNNC can be described by the first order autocatalytic equation

$$\frac{\mathrm{d}y}{\mathrm{d}t}=-10^{16.4}\exp\left(-\frac{210380}{RT}\right)y-10^{16.7}\exp\left(-\frac{171205}{RT}\right)y(1-y)$$

and that for the latter 50% mass-loss of HNNC described by the reaction equations

$$\frac{\mathrm{d}y}{\mathrm{d}t}=-10^{16.3}\exp\left(-\frac{169483}{RT}\right)y \quad (n=1) \text{ and } \frac{\mathrm{d}y}{\mathrm{d}t}=-10^{16.8}\exp\left(-\frac{165597}{RT}\right)y^{2.61} \quad (n\neq 1)$$

Keywords: first order autocatalytic reaction, HNNC, kinetics, TG

Introduction

Much attention has been paid to highly nitrated nitrocellulose containing 14.14% of nitrogen (HNNC) as a high energy 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 not the kinetics of the first order autocatalytic decomposition reaction of HNNC (14.14%N). In this work, we studied the kinetics of thermal decomposition processes of HNNC (14.14%N).

Experimental

Materials

The highly nitrated nitrocellulose containing 14.14% of nitrogen used in this work was prepared and purified at our institute.

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1418–2874/99/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

The thermal decomposition processes were studied by using the TG-DTA technique on a TA2100 TG-DTA instrument (TA Co., USA). The conditions of TG-DTA were as follows: sample mass, about 1 mg; heating rate, 18 K min^{-1}; atmosphere, a flowing rate of N_2 gas of 100 ml min^{-1}.

Kinetic equation and calculation of kinetic data

The solution of the first order autocatalytic equation for the thermal decomposition reaction of HNNC under non-isothermal conditions

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

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

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

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

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

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

$$\beta = \frac{dT}{dt} \tag{3}$$

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

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

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

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

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

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

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

$$\frac{\mathrm{d}z}{\mathrm{d}T}=\frac{k_1(T)+k_2(T)}{\beta}z-\frac{k_2(T)}{\beta} \tag{8}$$

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

For the corresponding first order homogeneous linear equation

$$\frac{\mathrm{d}z}{\mathrm{d}T}=\frac{k_1(T)+k_2(T)}{\beta}z \tag{9}$$

Separating its variables gives

$$\frac{\mathrm{d}z}{z}=\left[\frac{k_1(T)}{\beta}+\frac{k_2(T)}{\beta}\right]\mathrm{d}T \tag{10}$$

where T:$T_o \to T$; y:$y_o \to y$; z:$z_o \to z$ and $y_o=1$, $z_o=1$.

Integration of Eq. (10) gives

$$\int_{z_o}^{z}\frac{\mathrm{d}z}{z}=\int_{T_o}^{T}\left[\frac{k_1(T)}{\beta}+\frac{k_2(T)}{\beta}\right]\mathrm{d}T \tag{11}$$

$$\ln\frac{z}{z_o}=\frac{A_1}{\beta}\int_{T_o}^{T}\mathrm{e}^{-E_1/RT}\mathrm{d}T+\frac{A_2}{\beta}\int_{T_o}^{T}\mathrm{e}^{-E_2/RT}\mathrm{d}T \tag{12}$$

Setting

$$S_1(T)=\int_{T_o}^{T}\mathrm{e}^{-E_1/RT}\mathrm{d}T \tag{13}$$

and

$$S_2(T)=\int_{T_o}^{T}\mathrm{e}^{-E_2/RT}\mathrm{d}T \tag{14}$$

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

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

or

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

Setting

$$z_0 = V(T) \tag{17}$$

Eq. (16) becomes

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

$$\begin{aligned}\frac{\mathrm{d}z}{\mathrm{d}T} = \frac{\mathrm{d}V(T)}{\mathrm{d}T}\exp\left[\frac{A_1}{\beta}S_1(T) + \frac{A_2}{\beta}S_2(T)\right] + \\ V(T)\exp\left[\frac{A_1}{\beta}S_1(T) + \frac{A_2}{\beta}S_2(T)\right]\left[\frac{A_1}{\beta}S_1'(T) + \frac{A_2}{\beta}S_2'(T)\right]\end{aligned} \tag{19}$$

where

$$S_1'(T) = \mathrm{e}^{-\mathrm{E}_1/\mathrm{RT}} \tag{20}$$

$$S_2'(T) = \mathrm{e}^{-\mathrm{E}_2/\mathrm{RT}} \tag{21}$$

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

$$\frac{\mathrm{d}V(T)}{\mathrm{d}T} = -\frac{k_2(T)}{\beta}\exp\left\{-\left[\frac{A_1}{\beta}S_1(T) + \frac{A_2}{\beta}S_2(T)\right]\right\} \tag{22}$$

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

$$V(T_o) = 1 \tag{23}$$

Integrating Eq. (22), yields

$$\int_{\mathrm{V(T_o)}}^{\mathrm{V(T)}} \mathrm{d}V(T) = -\frac{1}{\beta}\int_{\mathrm{T_o}}^{\mathrm{T}} k_2(T)\exp\left\{-\left[\frac{A_1}{\beta}S_1(T) + \frac{A_2}{\beta}S_2(T)\right]\right\}\mathrm{d}T \tag{24}$$

and

$$V(T) = 1 - \frac{1}{\beta}\int_{\mathrm{T_o}}^{\mathrm{T}} k_2(T)\exp\left\{-\left[\frac{A_1}{\beta}S_1(T) + \frac{A_2}{\beta}S_2(T)\right]\right\}\mathrm{d}T \tag{25}$$

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

$$z = \left(1 - \frac{1}{\beta}\int_{\mathrm{T_o}}^{\mathrm{T}} k_2(T)\exp\left\{-\left[\frac{A_1}{\beta}S_1(T) + \frac{A_2}{\beta}S_2(T)\right]\right\}\mathrm{d}T\right)\exp\left[\frac{A_1}{\beta}S_1(T) + \frac{A_2}{\beta}S_2(T)\right] \tag{26}$$

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

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

This is the solution of the first order autocatalytic kinetic equation under non-isothermal conditions. Equation (27) describes the temperature dependence of the concentration for the first order autocatalytic reaction before the inflection point in the TG curve (for HNNC, the point corresponds to about 50% of mass-loss).

The solution of the kinetic equation for the thermal decomposition in the deceleration period under non-isothermal conditions

The rate equation for n^{th} order for describing the deceleration period after the inflection point in the TG curve (for HNNC, the point corresponds to the latter 50% of mass-loss) 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

$$k_3(T)=A_3e^{-E_3/RT} \quad (29)$$

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

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

Integration Eq. (30), yields

$$\int\limits_{1}^{y}y^{-n}dy=-\frac{A_3}{\beta}\int\limits_{T_o}^{T}e^{-E_3/RT}dT \quad (31)$$

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

Setting that

$$S_3(T)=\int\limits_{T_o}^{T}e^{-E_3/RT}dT \quad (33)$$

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

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

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

Equations (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 mass-loss in the TG 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

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

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

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

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

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

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

where

$$Q(T_i) = \frac{A_1}{\beta}S_1(T_i) + \frac{A_2}{\beta}S_2(T_i) =$$
$$= Q(T_{i-1}) + \frac{A_1}{\beta}\int_{T_{i-1}}^{T_i} e^{-E_1/RX}dX + \frac{A_2}{\beta}\int_{T_{i-1}}^{T_i} e^{-E_2/RX}dX = Q(T_{i-1}) + \frac{A_1EX1_i + A_2EX2_i}{\beta} \tag{40}$$

where

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

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

$$W(T_i) = W(T_{i-1}) + \frac{A_2}{\beta}\int_{T_{i-1}}^{T_i} \exp\left\{-\left[\frac{E_2}{RX} + Q(X)\right]\right\} dX = W(T_{i-1}) + \frac{A_2}{\beta} WX_i \tag{43}$$

where

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

We worked out programs by using Powell's optimization method [4] 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 method [5] is used in the one-dimension searching of the Powell's method.

The objective function of Eq. (34) is

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

The objective function of Eq. (35) is

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

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, ···, 41) 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 TG curve (T_i, Y_i; i=1, 2, ···, 28) and that of the remaining part (T_i, Y_i; i=29, ···, 41) are taken from the TG-DTA curve in Fig. 1.

Fig. 1 Typical TG and DTA curves for HNNC (14.14% N) at a heating rate of 18 K·min^{-1}

Table 1 Results of analysis of the thermal decomposition data for HNNC (14.14% N) by Eqs (27), (34) and (35)

y	Eq.	E_1/ kJ mol^{-1}	E_2/ kJ mol^{-1}	A_1/ s^{-1}	A_2/ s^{-1}	E_3/ kJ mol^{-1}	A_3/ s^{-1}	n	SD*
1.00–0.50	(27)	210.4	171.2	$10^{16.4}$	$10^{16.7}$				0.0394
0.50–0.03	(35) (n=1)					169.5	$10^{16.3}$		0.0570
	(34) (n≠1)					165.6	$10^{16.8}$	2.61	0.0146

* SD: Standard deviation; 0.0394, 0.0570 and 0.0146 are the values of SD corresponding to functions F_1, F_2 and F_3, respectively

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 TG curve for the initial 50% of mass-loss of HNNC can be described by the first order autocatalytic equation

$$\frac{\mathrm{d}y}{\mathrm{d}t}=-10^{16.4}\exp\left(-\frac{210380}{RT}\right)y-10^{16.7}\exp\left(-\frac{171205}{RT}\right)y(1-y)$$

and that for the latter 50% mass-loss of HNNC described by the reaction equations

$$\frac{\mathrm{d}y}{\mathrm{d}t}=-10^{16.3}\exp\left(-\frac{169483}{RT}\right)y \qquad (n=1)$$

and

$$\frac{\mathrm{d}y}{\mathrm{d}t}=-10^{16.8}\exp\left(-\frac{165597}{RT}\right)y^{2.61}\quad (n\neq 1)$$

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This work was supported by the Science and Technology Foundation of the National Defence Key Laboratory of Propellant and Explosive combustion of China.

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