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2,4,6-TRINITROTOLUENE THERMAL DECOMPOSITION: KINETIC PARAMETERS DETERMINED BY THE ISOTHERMAL DIFFERENTIAL SCANNING CALORIMETRY TECHNIQUE

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ABSTRACT

The isothermal differential scanning calorimetry technique is used to determine kinetic parameters for the thermal decomposition of 2,4,6-trinitrotoluene (TNT). Values for the activation energy and pre-exponential factor are presented. An analysis of the thermochemical induction period data is presented which allows calculation of the activation energy of the induction reaction.

INTRODUCTION

The compound 2,4,6-trinitroluene undergoes a thermochemical decomposition in its molten state. The kinetics of this thermal decomposition process were studied by a differential scanning calorimeter operated isothermally (isothermal DSC). Repeated isothermal DSC analyses within the 245–269°C range revealed that molten TNT shows a temperature dependent induction period prior to its exothermic decomposition. The induction period's time dependence upon temperature plus the activation energy of the induction period were determined, as were the reaction order, rate constants, and activation energy of the exothermic decomposition. Previous kinetic parameter values for TNT thermal decomposition were primarily determined by gas evolution or weight loss techniques (Table 2). Determination of kinetic parameters by the isothermal DSC method offers the advantages of being simple, rapid, and easily adaptable to induction period kinetic analysis.

EXPERIMENTAL

Apparatus

All measurements were made with a Perkin-Elmer Model DSC-1 differential scanning calorimeter. TNT samples were sealed in aluminum cells, Perkin-Elmer Part Number 219-0062. A Perkin-Elmer Sealer Assembly, Part Number 219-0061, was used to cold weld the cell lid to the pan.

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Samples

The TNT used was prepared and purified using a previously developed method[1].

Procedure

The average and differential temperature settings of the instrument were calibrated using a tin standard (m.p. 222°C). The instrument with an empty sealed cell on the reference support was pre-heated to the desired operating temperature for each analysis. When equilibrium was reached, a loaded cell (4.05±0.05 mg of TNT) was placed on the sample support. The time of placement was noted on the recorder chart for induction period analysis, and the TNT was allowed to thermally decompose at the indicated temperature. The data were processed using the techniques described in the Results and Discussion section of this paper.

RESULTS AND DISCUSSION

The thermal decomposition of molten TNT was studied by plotting heat evolution versus time data from isothermal DSC analysis. Isothermal DSC analysis of thermochemical TNT decomposition revealed a relatively long induction period (A) followed by exothermic acceleratory (B) and decay (C) phases. This decomposition is apparently catalyzed by an intermediate product formed in the induction period[2,3]. A generalized TNT decomposition curve is shown in Fig. 1.

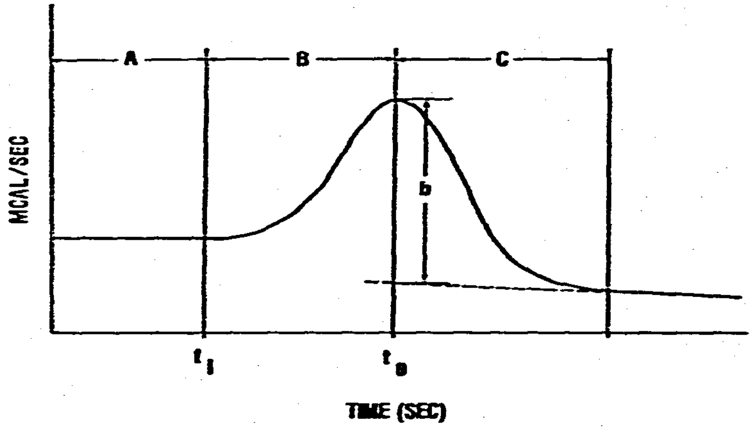

Fig. 1. A generalized sample of an isothermal DSC curve resulting from TNT thermochemical decomposition. The induction period (*A*) is followed by exothermic acceleratory (*B*) and decay (*C*) phases. t_I represents the length of the induction period. t_0 is the zero time for the decay phase and b is the recorder deflection corrected for the baseline of the decay phase.

The mathematical treatment of the data was based on previously published techniques[4,5]. The baseline established at the end of the decay phase (C) was extrapolated back to the point where the heat evolution rate was at a maximum; at this point, the time was taken to be zero (t_0), and the deflection of the decomposition curve from the baseline was measured as the quantity b. The recorder deflection, b, was then measured at regular time intervals until the end of the decay period and Simpson's Rule was used to calculate the total area under the decay curve (A_T). Fractional areas (A_n) at specific time intervals (n) were determined as a portion of the total area measurement; therefore, the fraction reacted (X) after each time interval is defined by eqn (1).

$$X = A_n/A_T \tag{1}$$

The reactant fraction remaining at the end of each specific time interval is then $1-X$, and a general rate expression for the decomposition can be written:

$$\mathrm{d}X/\mathrm{d}t = k(1-X)^n \tag{2}$$

The baseline deflection b is directly proportional to the reaction rate[5], or:

$$\alpha b = \mathrm{d}X/\mathrm{d}t \tag{3}$$

Equating eqns (2) and (3), we obtain:

$$\alpha b = k(1-X)^n \tag{4}$$

$$b \ = k/\alpha(1-X)^n \tag{5}$$

Taking the natural logarithm of both sides of eqn (5) gives eqn (6).

$$\ln b = \ln (k/\alpha) + n \ln (1-X) \tag{6}$$

The order for the thermochemical TNT decomposition is provided by the slope, n, obtained when $\ln b$ is plotted as a function of $\ln (1-X)$ (Fig. 2).

The TNT decomposition was found to be first order. For a first order reaction, the rate constant, k, is taken from the slope ($-k$) obtained when $\ln b$ is plotted against time (Fig. 3).

The energy of activation (E_a) was found in the standard manner by plotting $\ln k$ versus the absolute temperature reciprocal (Fig. 4). In this plot the slope is $-E_a/R$ and the y-intercept is $\ln Z$; from these graphical parameters the activation energy and the pre-exponential factor (Z) were determined.

The reaction order, rate, activation energy and pre-exponential factor are all obtained by analyzing the decay portion (C) of the decomposition curve. Two additional kinetic parameters were obtained from analysis of the induction portion (A) of the decomposition curve; these parameters are induction time and the activation energy (E_{aI}) of the induction reaction.

Induction time is defined as the time elapsed from the placement of the sample pan onto the sample support until the initial deflection of the decomposition curve from the baseline established by the induction (A) portion of the curve.

The induction reaction activation energy (E_{aI}) is ascertained by plotting the natural logarithm of the induction time (t_I) versus the absolute temperature reciprocal[6]. Several assumptions are made in the induction period data analysis.

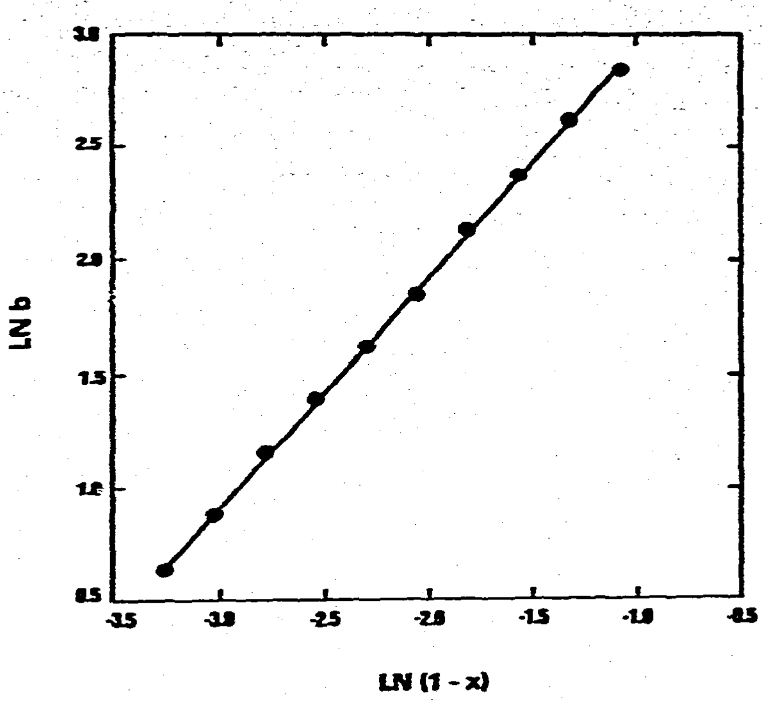

Fig. 2. Order plot for thermochemical TNT decomposition at 263 °C, $n = 1.01$.

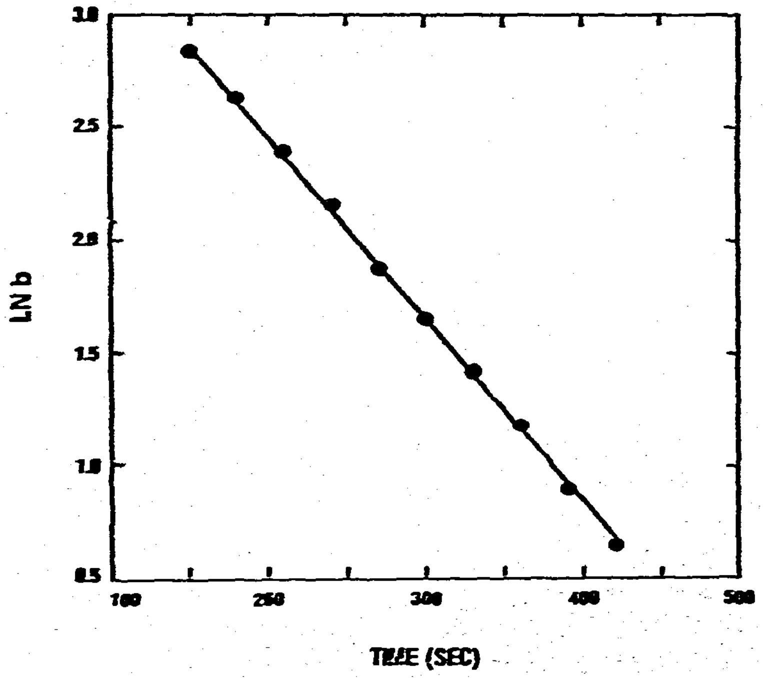

Fig. 3. First-order plot of the TNT sample illustrated in Fig. 2. TNT thermochemical decomposition at 263 °C, $k = 8.22 \times 10^{-3}$ sec^{-1}.

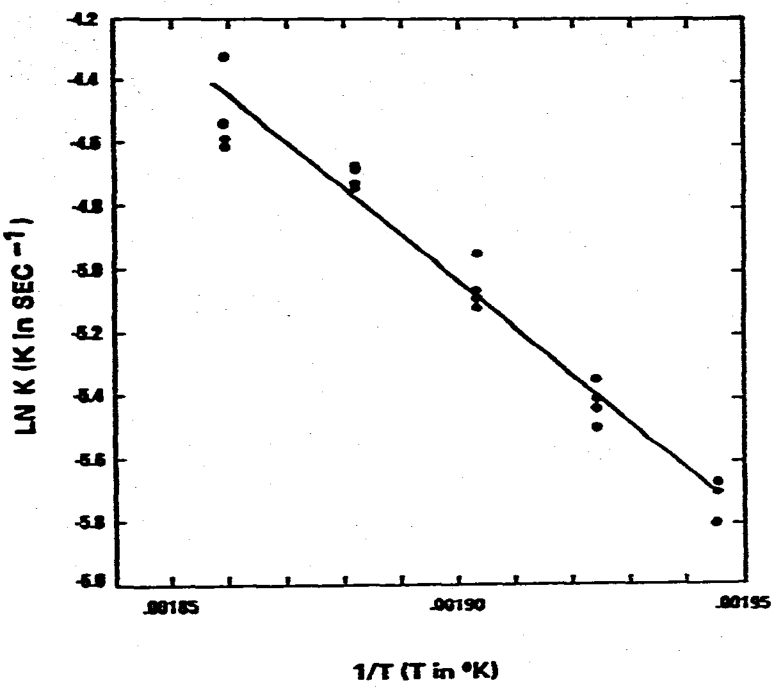

Fig. 4. Arrhenius plot of all isothermal DSC data obtained from the decay phase of TNT thermochemical decomposition. $E_a = 29.4 \pm 1.4$ kcal mol^{-1}.

The thermochemical decomposition of TNT is assumed to be autocatalytic, resulting from a small concentration of a catalytic substance (I) being formed during the induction process. The concentration of I is likely small enough to allow the following approximation:

$$di/dt = \Delta i/\Delta t \tag{7}$$

where i is the mole fraction of catalyst I.

Because no I is present at the beginning of the induction period,

$$\Delta i/\Delta t = i_I/t_I \tag{8}$$

where i_I is the total concentration of I formed by the end of the induction period, and t_I is the total length of the induction period in seconds.

A general rate expression for the induction process is:

$$di/dt = k(1-i)^n \simeq k. \tag{9}$$

Because I is present only in catalytic amounts, eqn (9) is a valid approximation and from eqns (7), (8), and (9):

$$k = i_I/t_I \tag{10}$$

Taking the natural logarithm of the Arrhenius equation gives equation (11).

$$\ln k = -E_{aI}/RT + \ln Z \tag{11}$$

From eqns (10) and (11)

$$\ln i_I - \ln t_I = -E_{aI}/RT + \ln Z \tag{12}$$

or,

$$\ln t_I = E_{aI}/RT + (\ln i_I - \ln Z) \tag{13}$$

A plot of $\ln t_I$ versus $1/T$ provides E_{aI}/R as the slope, from which E_{aI} is obtained (Fig. 5). The intercept yields the ($\ln i_I - \ln Z$) term and thus renders the values of i_I and Z inaccessible.

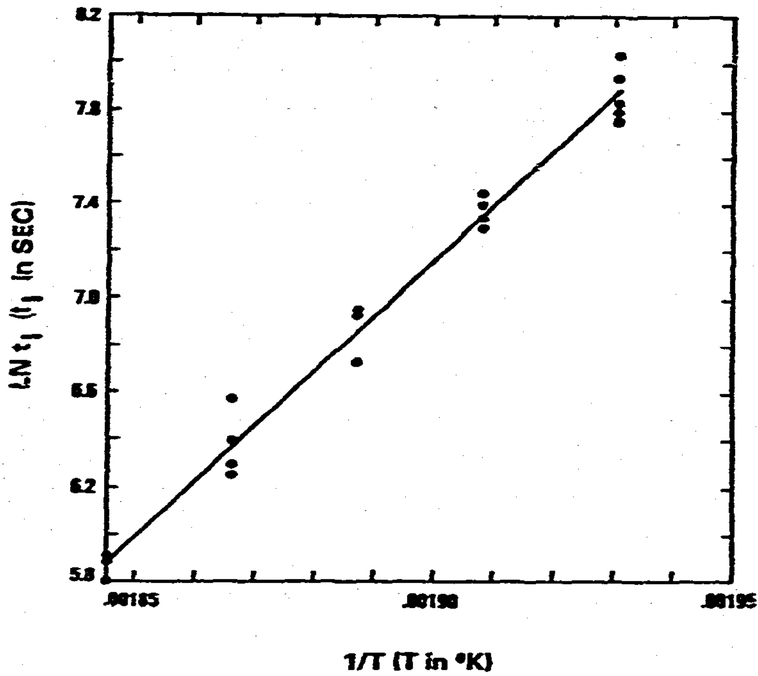

Fig. 5. Arrhenius plot of all isothermal DSC data obtained from the induction period of TNT thermochemical decomposition. $E_{aI} = 46.5 \pm 1.5$ kcal mol^{-1}.

The decomposition of TNT was studied by isothermal DSC over a temperature range of 245–269°C. The results were calculated as outlined and are given in Table 1.

TABLE 1

TNT THERMAL DECOMPOSITION KINETIC PARAMETERS (245–269°C)

Order	0.97 ± 0.07
Pre-exponential factor (sec^{-1})	$10^{9.9}$
Activation energy (kcal mol^{-1})	29.4 ± 1.4
Induction activation energy (kcal mol^{-1})	46.5 ± 1.5

A comparison of our results by the isothermal DSC method with those of other investigators is depicted in Table 2.

TABLE 2

COMPARISON OF
TNT THERMAL DECOMPOSITION KINETIC PARAMETERS REPORTED BY VARIOUS INVESTIGATORS

Investigators	*Z* (*sec*$^{-1}$)	*E_a* (*kcal mol*$^{-1}$)	*Temp. range* (°C)
R. Robertson[7]	—	25.0	140–180
A. J. B. Robertson[3]	$10^{11.4}$	34.4	275–310
T. Urbanski and T. Rychter[8]	—	14.0	390–450
S. Roginsky[9]	—	25.0	—
M. Cook and M. Abegg[10]	$10^{12.19}$	43.4	237.5–276.8
Yu. Ya. Maksimov[11]	—	31.5	280–320
This study	$10^{9.9}$	29.4	345–269

In this study, no attempt was made to separate heat of vaporization from heat of decomposition, but the relatively low vapor pressure of TNT even at the highest temperature analysis (calculated 102 torr[10] at 269 °C) implies that the heat evolved from vaporization is small compared to the heat of decomposition.

CONCLUSIONS

The thermal decomposition kinetics of TNT can be determined simply and rapidly with the isothermal DSC method. Values for the activation energy and pre-exponential factor were obtained and fit within the range reported previously using other techniques.

An analysis of induction time data provides the activation energy for the induction reaction. This kinetic parameter is not readily accessible from gas evolution or weight loss data. The induction period analysis technique will be used for planned studies designed to elucidate the TNT thermal decomposition mechanism.

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