

## **NON-LINEAR LEAST-SQUARES FIT OF NON-ISOTHERMAL THERMOANALYTICAL CURVES. REINVESTIGATION OF THE KINETICS OF THE AUTOCATALYTIC DECOMPOSITION OF NITRATED CELLULOSE**

N. EISENREICH and A. PFEIL

*Fraunhofer-Institut für Treib- und Explosivstoffe, 7507 Pfinztal 1 (F.R.G.)*

(Received 23 June 1982)

### **ABSTRACT**

The thermal decomposition of highly nitrated nitrocellulose was reinvestigated by non-isothermal techniques combining TG, quantitative DTA, IR and Raman. From a non-linear direct search least-squares fit of the entire reaction interval, kinetic parameters were derived. The best fit was obtained by first-order autocatalytic and second-order simple kinetics. The decomposition is a two-step process involving a stable intermediate.

### **INTRODUCTION**

A detailed knowledge of the thermal decomposition of nitrated cellulose (NC) is highly desirable to optimize the conditions of storage (ageing), ignition and combustion. This is particularly evident from the fact that all these compounds undergo autocatalysis. The reaction is complicated [1,2], producing a variety of products [2–6] involving a discontinuity in the rate of reaction as a function of temperature [6]. As a result, data in the literature are somewhat limited and contradictory conclusions have been drawn from the kinetics of decomposition.

This study differs from the previous work as it uses a non-isothermal approach. It will be shown that this approach has certain advantages in the study of an autocatalytic decomposition. Compared with the isothermal method, it extends the temperature range to include the entire reaction interval. The least-squares fit derives kinetic parameters which relate to the entire reaction interval thereby providing a better basis to test the validity of the proposed rate laws.

This work combines the methods employed in the previous studies to characterize the reaction interval, viz. change in weight, heat of reaction and vibrational spectra to monitor the appearance and disappearance of specific species.

## KINETICS

The autocatalytic equation for the thermal decomposition of NC under isothermal conditions [1,6] is

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

where  $y$  is the fraction of the unreacted reagent,  $(1-y)$  the fraction of reaction that has occurred,  $T$  the temperature and  $t$  the time.  $k_1(T)$  and  $k_2(T)$  are the rate constants of the first-order autocatalytic equation at the temperature  $T$ , defined by

$$k(T) = z \exp(-E/RT) \quad (2)$$

where  $z$  is the pre-exponential factor and  $E$  the activation energy.  $k_1$  denotes the first-order rate constant and  $k_2$  that of the autocatalytic reaction involving the reaction products. The solution of eqn. (1) is

$$y(t) = \frac{k_1 + k_2}{k_2 + c_0 \exp(k_1 + k_2)t} \quad (3)$$

where  $c_0$  denotes the integration constant and is given by

$$c_0 = \frac{k_1 + k_2(1-y_0)}{y_0} \quad (4)$$

$y_0$  being the fraction of the unreacted reagent at  $t = 0$ .

Equation (4) visualizes the effect of  $(1-y_0)$ , formed during the heating of the sample to the isothermal working temperature, on the course of the autocatalytic reaction. Even if the conversion is small, the effect is pronounced if  $k_2$  is large with respect to  $k_1$ . This, however, is expected for highly nitrated polymers like nitrocellulose. As a consequence, at higher temperatures, the numerical evaluation of kinetic constants is rather limited due to the loss of information on  $k_1$ , even if the degree of conversion is accurately accounted for [7].

In contrast, the non-isothermal experiment starts at a temperature where the formation of products is zero. Since the span of the temperature interval is limited only by the range of the instrument, the complete reaction interval can be recorded and analyzed as a whole. In this experiment, the sample is subject to a linear temperature rise defined by

$$dt = \frac{dT}{\beta} \quad (5)$$

where  $\beta$  is the linear heating rate.

Inserting eqn. (5) into eqn. (1), the solution of the differential equation is

$$y(T) = \frac{\exp\{[(-z_1/\beta)S_1(T)] - [(z_2/\beta)S_2(T)]\}}{1 - (1/\beta) \int k_2(T) \exp\{[(-z_1/\beta)S_1(T)] - [(z_2/\beta)S_2(T)]\} dT} \quad (6)$$

where  $S(T)$  is the integral of the Arrhenius function

$$S_1(T) = \int \exp(-E_1/RT) dT \quad (7)$$

$$S_2(T) = \int \exp(-E_2/RT) dT \quad (8)$$

Equation (6) describes the temperature dependence of the concentration for an autocatalytic reaction of the first order. We used eqn. (6) to analyze the first part of the experimental thermoanalytical curve of NC.

The remaining part, separated from the first part by the discontinuity, was analyzed by simple kinetics. The rate equation for the  $n$ th order is

$$\frac{dy}{dt} = -k_3(T)y^n \quad (9)$$

where  $k_3$  is the rate constant of the decomposition process defined by

$$k_3 = z_3 \exp(-E_3/RT) \quad (10)$$

Inserting eqn. (5) into eqn. (9), the solution is

$$y(T) = \left[ 1 + \frac{(n-1)z_3}{\beta} S_3(T) \right]^{1/(1-n)} \quad (11)$$

$$S_3(T) = \int \exp(-E_3/RT) dT \quad (12)$$

The kinetic parameters were determined by fitting eqns. (6) and (11) to the experimental thermoanalytical curves by a non-linear least-squares program [8]. The fit parameters of eqn. (6) were  $E_1$ ,  $E_2$ ,  $z_1$ ,  $z_2$  and for eqn. (11)  $E_3$ ,  $z_3$  and  $n$ . The quantitative DTA curves were normalized with respect to the area and fitted by the first derivative of eqns. (6) or (11).  $S(T)$  was calculated using the exponential integral [9]. The integral involved in eqn. (6) was computed numerically, applying Simpson's rule.

The usefulness of this fit program in the treatment of thermoanalytical curves was demonstrated in an earlier publication [10].

## METHODS

The decomposition of NC (1.1% H<sub>2</sub>O, 13.3% N), which contained no stabilizer, was studied in air by simultaneous TG/DTA (Mettler) and quantitative DTA (DuPont 990). The heating rate was 0.5 K min<sup>-1</sup> and the sample weight 5 and 10 mg. Under these conditions, no self-heating or deflagration of the NC samples occurred (11).

The progress of the decomposition was recorded by monitoring the concentration of the functional groups OH, CH<sub>2</sub>, CO and ONO<sub>2</sub>. The reaction was quenched at a series of temperatures chosen from the interval 400–500 K and the residual part of the sample analyzed by IR (Perkin-Elmer 580B) and Raman (Coderg LRT 800, Ar<sup>+</sup> laser excitation at 514.5 nm) techniques. A Beer's law relationship was assumed between functional group

concentration and peak height (IR absorbance) or peak area (Raman intensity). The peak height and peak area were normalized either with respect to the  $\text{CH}_2$  group intensity at  $2925\text{ cm}^{-1}$  (assumed to be constant up to 443 K) or with respect to weight.

## RESULTS

Figures 1–5 depict the reaction interval of the NC.

Figure 1 qualitatively describes the structural degradation by a series of IR spectra. The numbers indicate the temperatures at which the decomposition of the sample was quenched. The figure reveals the decline of the  $\text{ONO}_2$  (centered at 836, 1283 and  $1656\text{ cm}^{-1}$ ) and  $\text{CH}_2$  ( $2925$  and  $2970\text{ cm}^{-1}$ ) bands and the growth of the OH ( $3410\text{ cm}^{-1}$ ) and CO ( $1742\text{ cm}^{-1}$ ) bands throughout the reaction interval.

Similar results were obtained from the Raman spectra. However, starting at about 50% conversion, a fast-growing strongly fluorescing background appeared which prevented the further registration of Raman spectra. A similar appearance in the IR is the rapid growth of a strongly absorbing background and the considerable broadening of the band profiles.

Figures 2 and 3 show the concentration profiles of the total weight (Fig. 2) and IR absorption of the CO group (Fig. 3). These profiles also characterize the change of the  $\text{ONO}_2$  and OH functional groups. A further common property is the point of inflection in the experimental curves at about 50% conversion (open circles in Figs. 2 and 3). At this point, the calculated curves exhibit a discontinuity in the reaction rate. The discontinuity is marked in Figs. 2 and 3 by the intersection of the solid lines (autocatalytic kinetics) and dotted lines (simple kinetics).

The product formed at the discontinuity was isolated and characterized by

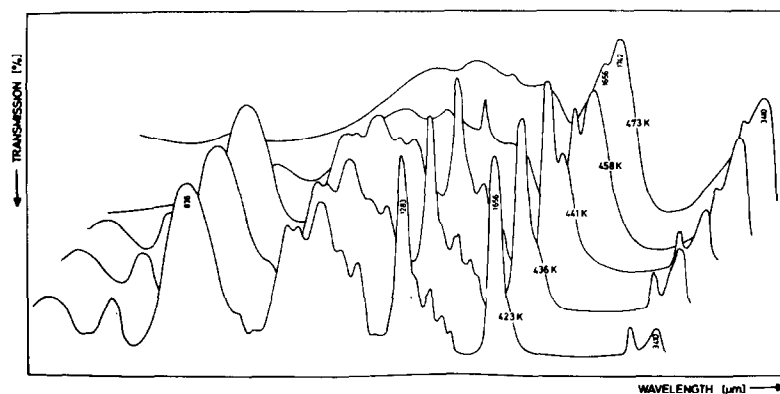


Fig. 1. IR spectra of partially decomposed NC samples quenched at the indicated temperatures.

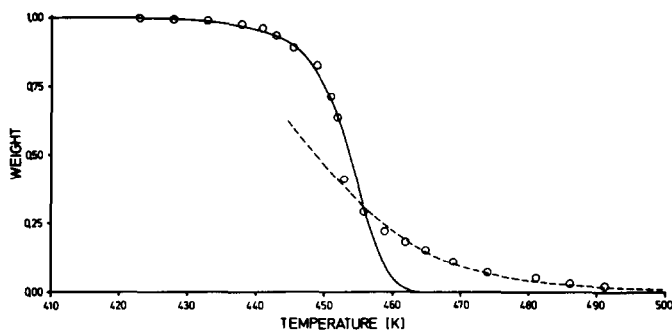


Fig. 2. TG of 5 mg NC in air, heating rate  $0.5 \text{ K min}^{-1}$  (weight of the residue subtracted).

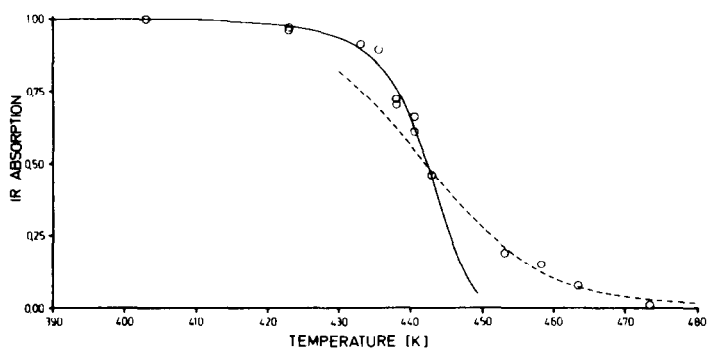


Fig. 3. CO absorbance (normalized, difference to 1) of partially decomposed NC, decomposition quenched at indicated temperatures.

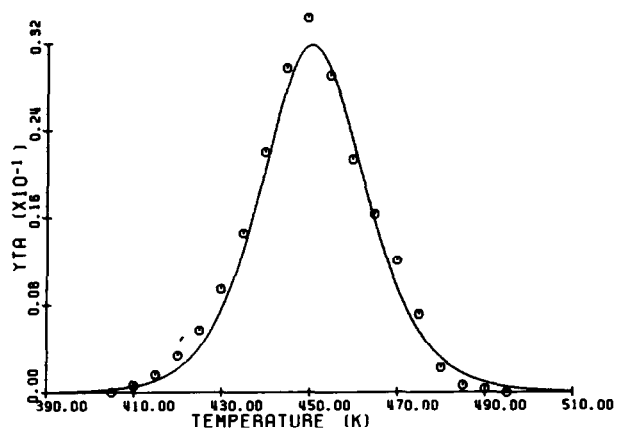


Fig. 4. Quantitative DTA in air of 1 mg partially decomposed NC, decomposition quenched at the discontinuity (50% conversion). Heating rate  $0.5 \text{ K min}^{-1}$ .

DTA and IR. Figure 4 depicts the quantitative DTA curve. The curve is of symmetric shape, which is typical for second-order kinetics [7]. The reaction order determined from a fit of the derivative of eqn. (8) was  $n = 1.96$ . The IR showed a transient band at  $1578 \text{ cm}^{-1}$ .

Figure 5 displays the DTA curve of undecomposed NC. It shows the

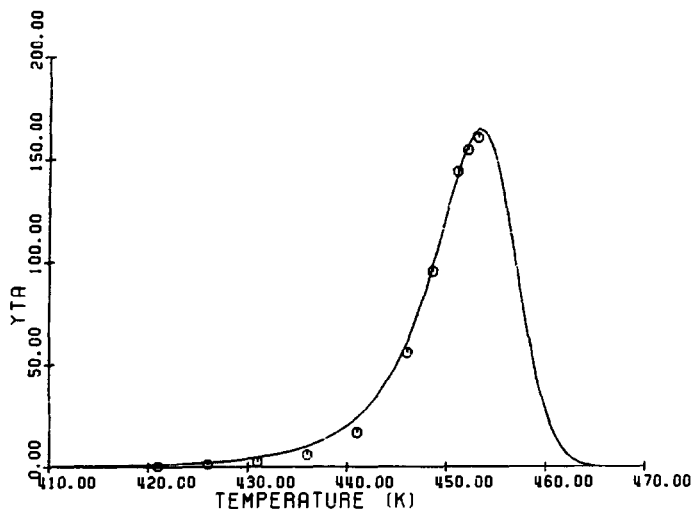


Fig. 5. Quantitative DTA of 1 mg NC in air (autocatalytic reaction). Heating rate  $0.5 \text{ K min}^{-1}$ .

TABLE 1

Kinetic parameters of the first-order autocatalysis reaction. Heating rate  $0.5 \text{ K min}^{-1}$ .

Method	Weight (mg)	$E_1$ (kcal mole $^{-1}$ )	$\log z_1$	$E_2$ (kcal mole $^{-1}$ )	$\log z_2$	Standard deviation (%)	Notes
TG	100	47	19	31	12		1
TG	5	41.7	16.3	42.2	17.5	7.3	2
TG	5	42.5	16.4	41.7	17.5	0.7	3
TG	5	42.6	16.6	41.9	17.5	1.0	
DTA	5	42.1	16.5	40.9	17.4	1.4	4
DTA	5	40.4	15.6	41.4	17.3	5.9	
IR	10	41.6	16.6	39.8	16.6	7.1	5
IR	10	42.6	16.9	39.5	16.8	7.7	6
IR	10	42.6	16.8	39.4	16.8	7.6	7
IR	10	41.0	16.4	39.8	16.9	4.2	8
IR	10	40.1	16.1	40.5	17.0	6.0	9
Raman	10	37.9	15.4	41.9	17.0	6.3	10

1. Isothermal, from ref. 6. 2. Isothermal, from ref. 7. 3. Sample deflagrated at the discontinuity point. 4. Heating rate  $20 \text{ K min}^{-1}$ . 5.  $836 \text{ cm}^{-1}$ . 6.  $1283 \text{ cm}^{-1}$ . 7.  $1656 \text{ cm}^{-1}$ . 8.  $1742 \text{ cm}^{-1}$ . 9.  $3410 \text{ cm}^{-1}$ . 10.  $843$  and  $1284 \text{ cm}^{-1}$ .

profile of the evolved heat up to 50% conversion. Compared with Fig. 4, the curve is characterized by the asymmetric shape and the later start of the heat evolution.

Tables 1 and 2 summarize the kinetic parameters which gave the best fit between the experimental values and the curves calculated from eqns. (6) and (11), respectively. For the calculation of  $k_3$  in Table 2, the reaction order  $n = 2$  was used. Over the temperature range investigated,  $k_3$  was found to be of the same order of magnitude as  $k_2$ , whereas  $k_1$  was less by one order. The rates are compared in Fig. 6.

The decomposition quenched at 500 K yielded a residue of about 20% of the initial weight. Elementary analysis, DTA and IR spectra characterized

TABLE 2  
Kinetic parameters of order simple kinetics

Method	Heating rate (K min <sup>-1</sup> )	Weight (mg)	$E_3$ (kcal mole <sup>-1</sup> )	log $z_3$	Standard deviation (%)
TG <sup>a</sup>	Isothermal		31.4	11.4	
TG	0.5	5	43.2	17.9	10.5
DTA	0.5	10	48.4	20.3	13.3
IR (836)	0.5	10	40.7	17.0	8.0
IR (1283)	0.5	10	48.8	20.6	10.8
IR (1656)	0.5	5	35.4	13.7	14.0
IR (1742)	0.5	10	47.1	20.1	10.6

<sup>a</sup> From ref. 6.

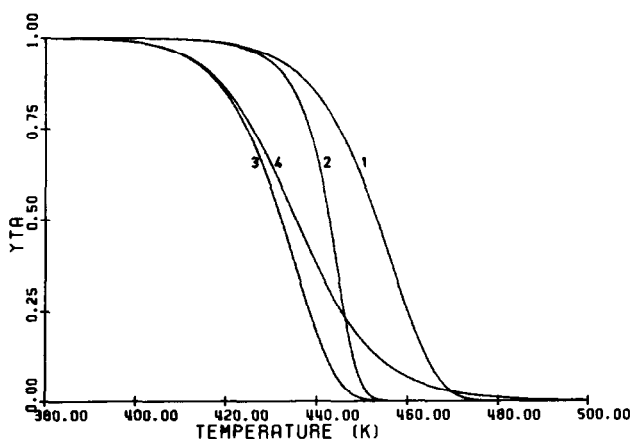


Fig. 6. Comparison of the rates. 1,  $k_1$  (simple first-order); 2,  $k_1, k_2$  (first-order autocatalytic); 3,  $k_2$  (simple first-order); 4,  $k_2$  (simple second-order). (log  $z_1 = 16.4$ , log  $z_2 = 17.4$ ,  $E_1 = E_2 = 41.0$  kcal mole<sup>-1</sup>.)

this residue as a charcoal-type material containing about 96% C. The material is similar to that isolated from the combustion of NC containing propellants in pressurized bombs [10].

## DISCUSSION

The non-isothermal results confirm that the thermal degradation of NC proceeds in two main steps [6,11]. Two rate laws are required to describe the decomposition process, first-order autocatalysis and simple second-order, both separated by a discontinuity. The discontinuity appears at about 50% conversion.

The two rate laws defined by eqns. (6) and (11) satisfactorily describe the decomposition process visualized by the synchronous profiles of the theoretical and experimental curves and the adequate fit expressed by the standard deviation in Tables 1 and 2.

A significant result in Table 1 is that the activation energies  $E_1$  and  $E_2$  of the autocatalytic process are equal within experimental error ( $E_1 = E_2 = 41$  kcal mole<sup>-1</sup>). This finding is in contrast to that of Manelis et al. [6]. Although the conversion rates ( $dy/dt$ ) calculated from Table 1 agree reasonably within the temperature range of their study, they found  $E_1$  and  $E_2$  to be different ( $E_1 = 47$ ,  $E_2 = 31$  kcal mole<sup>-1</sup>).

Manelis et al. [6] used isothermal techniques to deduce the parameters. The sample weights ranged from 50 to 600 mg and the temperature interval was 413–438 K. Though their sample was somewhat different (the nitrogen content was 12.6%), the discrepancy above must be caused by the different temperature interval and sample weight.

The dissociation energy of the O–NO<sub>2</sub> bond of simple nitrate esters ranges from 36 to 40 kcal mole<sup>-1</sup> [2–5,12,13]. For solid esters, a somewhat higher value is expected [5]. The equality of  $E_1$  and  $E_2$  suggests that the initial step, the cleavage of the CO–NO<sub>2</sub> bond, is the same for both the monomolecular ( $E_1$ ) and the catalyzed reaction ( $E_2$ ).

The order of magnitude of  $E_3$  indicates that cleavage of the O–NO<sub>2</sub> bond remains the primary step of the progressed decomposition after autocatalysis ran out. Further support is the linear relationship displayed by the parameters of Tables 1 and 2 in the plot of  $\log z$  against  $E$  (linear compensation effect) [7]. As is apparent from Table 2 and Figs. 2–4, the decomposition follows simple kinetics which is consistent with the results in ref. 6. However, the intensive background in both the IR and Raman spectra reflects the complex nature of the decomposition, which causes a complete degradation as evidenced by the high carbon content of the residue at 520 K.

The IR spectrum of the product isolated at the discontinuity is identical to the spectrum of a product obtained by Wolfrom et al. [2] from the combustion of NC at low pressures. The combustion produced a polymeric residue



in a yield of about 50%. They identified the product as a fragmented type of nitrated oxycellulose consisting mainly of a central core of unaltered nitrated anhydro-D-glucose units flanked by altered units.

Accordingly, the two main steps of the slow thermal decomposition of NC appear as an autocatalytic reaction producing this stable intermediate followed by a second-order carbonisation reaction which degrades the intermediate to the charcoal-type material. Both products are found in combustion reactions.

## REFERENCES

- 1 S. Roginski, *Phys. Z. UdSSR*, 1 (1932) 640.
- 2 M.L. Wolfrom, J.H. Frazer, L.P. Kuhn, E.E. Dickey, S.M. Olin, D.O. Hoffman, R.S. Bower, A. Chaney, E. Carpenter and P. McWain, *J. Am. Chem. Soc.*, 77 (1955) 6573.
- 3 G. Gelernter, L.C. Browning, S.R. Harris and C.M. Mason, *J. Phys. Chem.*, 60 (1956) 1260.
- 4 R.W. Philipps, C.A. Orlick and R. Steinberger, *J. Phys. Chem.*, 59 (1955) 1034.
- 5 L. Dauerman and Y.A. Tajima, *AIAA J.*, 6 (1968) 678, 1468.
- 6 G.B. Manelis, Y.I. Rubtsov, L.P. Smirnov and F.I. Dubovitskii, *Kinet. Katal.*, 3 (1962) 42.
- 7 N. Eisenreich, Dissertation, Technical University of Munich, 1978.
- 8 M.J.D. Powell, *Comput. J.*, 7 (1964) 155.
- 9 E. Koch, *Non-Isothermal Reaction Analysis*, Academic Press, London, 1977.
- 10 N. Eisenreich and A. Pfeil, *Thermochim. Acta*, 29 (1979) 305.
- 11 F. Paulik, J. Paulik and M. Arnold, *J. Therm. Anal.*, 12 (1977) 383.
- 12 J.B. Levy, *J. Am. Chem. Soc.*, 76 (1954) 3254.
- 13 J.A. Kerr, *Chem. Rev.*, 66 (1966) 465.