

THERMAL DECOMPOSITION OF ENERGETIC MATERIALS. PART 51. KINETICS OF WEIGHT LOSS FROM NITRATE ESTER POLYMERS AT LOW HEATING RATES

J.K. CHEN and T.B. BRILL *

Department of Chemistry, University of Delaware, Newark, DE 19716 (U.S.A.)

(Received 4 September 1990)

ABSTRACT

The kinetics of weight loss of six polymeric nitrate esters is described by the non-linear least-squares fit of non-isothermal TGA weight-loss curves. In the first 50% of weight loss, nitrocellulose (9.45%, 11.7%, and 13.4% nitrogen) and poly(vinyl nitrate) undergo first-order autocatalytic decomposition. Poly(glycidyl nitrate) and poly(nitratomethylmethyloxethane) exhibit simple first-order kinetics. The tendency to become autocatalytic follows the trend toward higher oxygen balance, higher viscosity, and the increased presence of secondary alkyl nitrate sites in the molecules.

INTRODUCTION

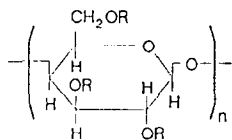
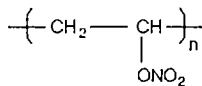
Studies of the decomposition of nitrocellulose under slow heating conditions ($dT/dt < 5^\circ\text{C min}^{-1}$) have been extensive [1–7]. For instance, the kinetics of weight loss measured by TGA reveals that the decomposition process initially follows a first-order rate law that may be associated with O–NO₂ homolysis as in reaction (1) [4,5]



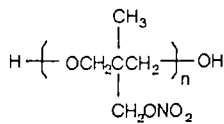
Autocatalysis, perhaps as a result of $\cdot\text{NO}_2$ reacting with $\text{RO}\cdot$, then becomes increasingly important. After about 50% of the weight is lost, a discontinuity occurs in the weight-loss curve and a second-order rate expression best describes the process [4,5]. This latter stage has been interpreted as indicating that backbone cleavage reactions are occurring [8].

Recently, the decomposition kinetics of thin films of nitrocellulose (NC), poly(vinyl nitrate) (PVN), poly(glycidyl nitrate) (PGN), and poly(nitromethylmethyloxethane) (NMMO) have been studied at heating rates exceeding $100^\circ\text{C sec}^{-1}$ [9]. The rate laws that describe the weight loss from NC at

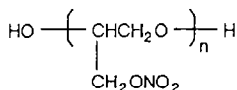
* Author for correspondence.

NC (R=H or NO₂)

PVN



NMMO



PGN

slow and fast heating rates are different. Unlike the first-order autocatalytic model that describes NC at low heating rates, the first 50% of weight lost at high heating rates is best described by a simple second-order power rate law. Because no previous kinetic studies of PVN, PGN and NMMO were found, comparisons of the high rate decomposition kinetics with low rate decomposition data could not be made for these compounds. Low heating rate TGA kinetics data would also enable more general comparisons to be made of the kinetics of decomposition of nitrate ester polymers. Therefore, this paper describes the kinetics of weight loss measured by TGA for three samples of NC that differ in the percent N, and for PVN, PGN and NMMO. The initial 50% of weight loss is considered. In this early part of the decomposition, the induction process is emphasized. The later stage of weight loss where the residue reactions dominate was not studied here.

EXPERIMENTAL

Samples of nitrocellulose were supplied by Y.P. Carignan of Picatinny Arsenal, NJ. PVN, PGN and NMMO were provided by A. Becuwe (SNPE, Le Bouchet, France), R.L. Willer (Thiokol, Elkton, MD), and G. Manser (Aerojet, Sacramento, CA), respectively.

Thermogravimetric analysis was conducted using a Dupont Instruments Model 951 TGA at 0.5 or 1°C min⁻¹ under Ar at a flow rate of 20 ml min⁻¹. Samples of 1.75–2.55 mg were used in all cases. The first-order weight-loss curves were fit by the non-linear regression subroutine RNSSQ contained in the International Mathematical and Statistical Library.

KINETIC MODELS

The first-order autocatalytic model that describes the TGA weight-loss curves during the thermal decomposition of NC at $dT/dt \leq 1^\circ\text{C min}^{-1}$ is

well known [2,4,5]. As a check on how our TGA methods compared with previous work, we reinvestigated samples of 13.4 %N NC for comparison with published data. The data, especially those of Eisenreich and Pfeil [4] on 13.3 %N NC, are fully reproducible in our laboratory. We employed the non-linear least-squares model for non-isothermal decomposition that they used. In their approach they searched directly for the least-squares fit of the temperature integral of the Arrhenius equation. Since multiple solutions of this integral are possible, we wished to determine whether their converged values were the appropriate ones. Therefore, the Coats and Redfern approximation [10] was used to obtain an initial guess of the solution. The final, converged values of the least-squares calculation were found to be the same as those of Eisenreich and Pfeil indicating that their direct search procedure had converged at the most reasonable solutions. Thus, no further elaboration of this published kinetic model is needed here. The weight-loss data for all samples of NC and the sample of PVN were analyzed by the model.

The weight-loss curves for PGN and NMMO were found not to require the first-order autocatalytic model. Only a simple first-order model was found to be necessary. In this model, the rate of weight loss, $d\alpha/dt$ is given by

$$d\alpha/dt = k(T)(1 - \alpha) \quad (2)$$

where α and $k(T)$ are defined by eqns. (3) and (4)

$$\alpha = (W_0 - W_t)/(W_0 - W_f) \quad (3)$$

$$k(T) = A e^{-(E/RT)} \quad (4)$$

If a linear heating rate is employed, then $dT/dt = \beta$. Therefore

$$\int_0^\alpha \frac{d\alpha}{(1 - \alpha)} = \frac{A}{\beta} \int_{T_0}^T e^{-(E/RT)} dT \quad (5)$$

Redefining $T_0 = 0$, the temperature integral $S(T)$ is given by

$$S(T) = \int_0^T e^{-(E/RT)} dT \quad (6)$$

Since eqn. (6) has no closed solution, it can be solved as an asymptotic expansion, eqn. (7), [10,11]

$$S(T) = \frac{RT^2}{E} e^{(-E/RT)} \left[1 - 2\left(\frac{RT}{E}\right) + 6\left(\frac{RT}{E}\right)^2 - 24\left(\frac{RT}{E}\right)^3 + \dots \right] \quad (7)$$

If only the first two terms of the expansion of eqn. (7) are considered [12] then

$$\ln\left(\frac{-\ln(1 - \alpha)}{T^2}\right) = \ln\left[\frac{AR}{\beta E} \left(1 - 2\left(\frac{RT}{E}\right)\right)\right] - \frac{E}{RT} \quad (8)$$

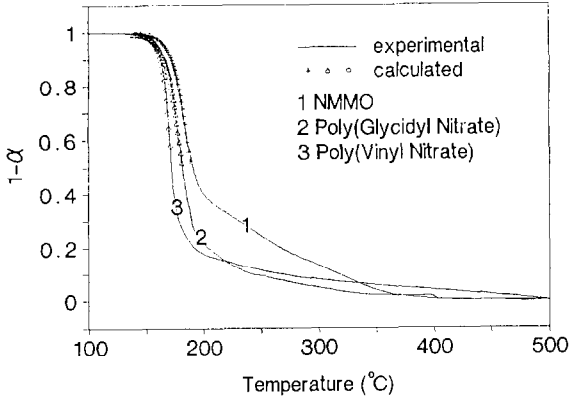


Fig. 1. The experimental and kinetically modelled TGA weight-loss curves for three nitrate ester polymers. The first 50% of conversion was modelled.

Using eqn. (8) to obtain an initial estimate of E and A , the non-linear least-squares method can then be used to solve eqn. (9) and obtain more accurate values of E and A

$$(1 - \alpha) = \exp \left[-\frac{ART^2}{\beta E} e^{-(E/RT)} \left(1 - 2\left(\frac{RT}{E}\right) + 6\left(\frac{RT}{E}\right)^2 - \dots \right) \right] \quad (9)$$

RESULTS

Figure 1 shows the weight-loss curves for NMMO, PVN and PGN. By using these data and those for 9.45%, 11.7% and 13.4 %N NC, Arrhenius plots were constructed from eqn. (8). Figure 2 shows these plots for PVN, PGN and NMMO. Figure 3 shows the plots for the three samples of NC.

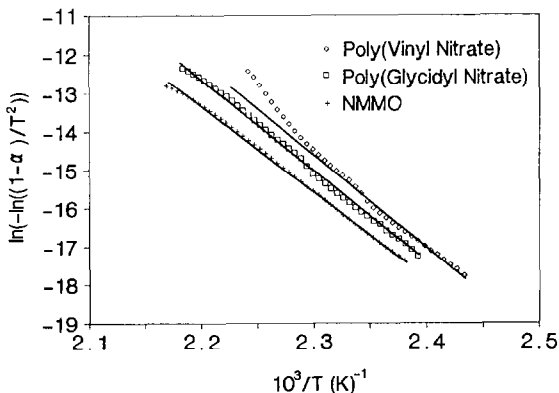


Fig. 2. Arrhenius plots for three nitrate ester polymers showing first-order behavior, except for PGN at higher temperature, where autocatalysis becomes important.

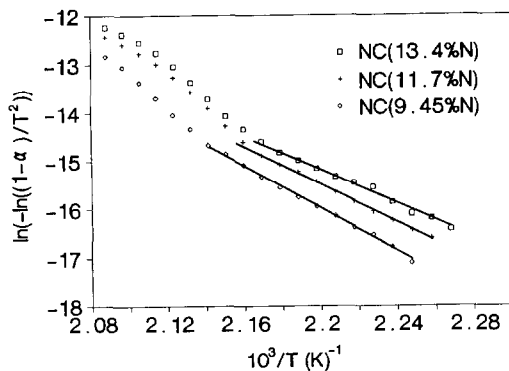


Fig. 3. Arrhenius plots for three nitrocellulose samples showing first-order behavior at lower temperature with autocatalysis becoming important at higher temperatures.

Note that NC and PVN follow first-order kinetics only in the low temperature range (138–160°C for PVN, 169–190°C for NC). The autocatalytic process then becomes important. This behavior requires the use of a first-order autocatalytic model to calculate the kinetic constants given in Table 1. On the other hand, PGN and NMMO follow simple first-order kinetics throughout the initial 50% of weight loss (144–180°C) without undergoing autocatalysis. The final E and A values in Table 1 were calculated from eqn. (9). The weight-loss curves calculated from these models are shown on Fig. 1 for comparison with the experimental data.

Three factors in these compounds may be responsible for their different kinetic behavior: the differences in phase, energy content (oxygen balance), and number of primary and secondary alkyl nitrate groups. With regard to the phase, NC and PVN are amorphous solids up to the decomposition temperature, whereas PGN and NMMO are viscous fluids at room temperature. The ease with which the gaseous products, especially NO_2 , can escape

TABLE 1

TGA kinetic parameters of nitrate ester polymers

Polymer	Heating rate (°C min ⁻¹)	First-order step		Autocatalytic step	
		E (kcal mol ⁻¹)	log A (sec ⁻¹)	E (kcal mol ⁻¹)	log A (sec ⁻¹)
NC(13.4 %N)	0.5	40.6	15.1	41.0	16.0
NC(11.7 %N)	0.5	40.8	15.2	41.1	16.0
NC(9.45 %N)	0.5	41.7	15.4	41.2	15.9
PVN	1.0	47.7	20.2	46.0	19.9
PGN	1.0	46.2	19.3		
NMMO	1.0	44.2	18.0		

the condensed phase would be expected to be greater for PGN and NMMO. Hence, the concentration of NO_2 may not build up to the level needed to create significant autocatalysis. The more rigid NC and PVN matrices may retain the NO_2 to a greater extent and enable autocatalysis to become important. Consistent with this, Phillips et al. [1] found that the decomposition of NC followed first-order kinetics below 200 mm Hg, but more complicated kinetics were followed at high pressures. The decomposition gases would be expected to escape from the sample more readily at lower pressure. Were this physical mechanism entirely responsible for the kinetics differences, the concentration of NO_2 in the gas phase would be expected to be higher for PGN and NMMO than for the other samples. This is not found experimentally [9], and illustrates the value of performing IR analysis of the near-surface products when conducting these types of experiments.

A second explanation for the apparently different kinetic behavior of these compounds upon thermolysis lies in the oxygen balance. Figure 3 shows that the deviation from first-order behavior of NC decreases as the oxygen balance (or percent N) decreases. The acceleratory effect of NO_2 on the degradation of the sample at higher temperature depends on a threshold amount of NO_2 in the sample being reached relative to the other products. Otherwise, the reaction might continue to follow global first-order behavior as suggested by reaction (1). PGN and NMMO have an even lower oxygen balance than 9.45 %N NC. On this basis they would be expected to tend toward the dominance of first-order kinetics, in accordance with what is found experimentally. Thus, it appears that the oxygen balance (amount of NO_2 available relative to the other products) may play a role in the reaction rate. A higher oxygen balance favors first-order autocatalysis while a lower oxygen balance favors simple first-order kinetics.

A third factor may be the position of the nitrate ester group on the backbone. The preferential site for nitration of NC is the primary alcohol [13]. Thus, the ratio of primary/secondary alkyl nitrate groups is higher in 9.45 %N NC than 13.4 %N NC. As the percent N in NC decreases, autocatalysis occurs to a lesser extent (Fig. 3) suggesting that autocatalysis is favored by the presence of the secondary nitrate groups. In keeping with this pattern, PVN, which possesses only secondary alkyl nitrate groups decomposes autocatalytically while PGN and NMMO, which possess only primary alkyl nitrate groups follow simple first-order kinetics.

All three of the above observations may be contributing factors in the different kinetics of decomposition of these nitrate ester polymers. However, the first-order or first-order autocatalytic models do not satisfactorily fit the weight-loss kinetics at heating rates exceeding $100^\circ\text{C sec}^{-1}$ [9], where a simple second-order expression was found to be necessary.

ACKNOWLEDGEMENTS

We are grateful to the Air Force Office of Scientific Research, Aerospace Sciences, for support of this work on AFOSR-89-0521. Samples of compounds were generously supplied by Y.P. Carignan, A. Becuwe, R. Willer and G. Manser.

REFERENCES

- 1 R.W. Phillips, C.A. Orlick and R. Steinberger, *J. Phys. Chem.*, 59 (1955) 1034.
- 2 G.B. Manelis, Y.I. Rubtsov, L.P. Smirnov and F.I. Dubovitskii, *Kinet. Katal.*, 3 (1962) 42.
- 3 A.A. Duswalt, *Thermochim. Acta*, 8 (1974) 57.
- 4 N. Eisenreich and A. Pfeil, *Thermochim. Acta*, 61 (1983) 12.
- 5 J.-J. Jutier and R.E. Prud'homme, *Thermochim. Acta*, 104 (1986) 321.
- 6 H.N. Volthamer and A. Fontijn, *Combust. Flame*, 41 (1981) 313.
- 7 For a review of product analysis studies see R.A. Fifer, *Fundamentals of Solid Propellant Combustion*, in K.K. Kuo and M. Summerfield (Eds.), *Prog. Astronaut. Aeronaut.*, 90 (1984) 177.
- 8 N. Eisenreich, H.H. Krause and A. Pfeil, *Thermochim. Acta*, 85 (1985) 395.
- 9 J.K. Chen and T.B. Brill, *Combust. Flame*, in press.
- 10 P. Murray and J. White, *J. Trans. Brit. Ceram. Soc.*, 54 (1955) 204.
- 11 G. Gyulai and E.J. Greenhow, *Thermochim. Acta*, 6 (1973) 239.
- 12 A.W. Coats and J.P. Redfern, *Nature*, 201 (1964) 68.
- 13 T.K. Wu, *Macromolecules*, 13 (1980) 74.