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Degradation of the Molecular Weight and Nitrate Ester Content of Cellulose Nitrate on Thermal Aging

H. R. Leider
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MASTER

June 1981

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CONTENTS

Abstract	1
Introduction	1
Experimental	1
Nitrate Ester Decomposition	2
Degradation in Molecular Weight	3
Discussion	4
Conclusions	7
Acknowledgements	7
References	8

Degradation of the Molecular Weight and Nitrate Ester Content of Cellulose Nitrate on Thermal Aging

ABSTRACT

Changes in molecular weight and nitrate ester content for cellulose nitrate (NC), either "pure" or as a constituent of PBX-9404, were determined as a function of time and temperature. Changes in the number-averaged molecular weight, $\bar{M}_n$, are described by the simple theory of random chain scission, and $\bar{M}_n$ is found to correlate well with nitrate ester loss. Significant differences are seen between NC aged in the isolated condition and aged as the binder in PBX-9404.

INTRODUCTION

We have recently reported on studies of the thermal stability of the high explosive PBX-9404,^{1,2} in which we concluded that decomposition of the cellulose nitrate binder (NC) was responsible for all the observed changes. Our results on gas evolution and weight loss were in general agreement with other reported results obtained under similar conditions³⁻⁵ and our kinetic description of the decomposition agreed with those determined in the same temperature range for materials containing NC.⁶⁻¹⁰

We have extended our previous work by carrying out additional thermal aging tests on "pure" cellulose nitrate up to 120°C and have examined the NC for changes in molecular weight and nitrate ester content. We show that the degradation in molecular weight of NC, either alone or as a constituent of PBX-9404, can be described using a simple model¹¹ and that the changes in molecular weight and in nitrate ester content are intimately connected.

EXPERIMENTAL

Cellulose nitrate from the same lot used to formulate the PBX-9404 in our earlier work was put into stainless steel containers identical to those previously described.¹ They were then stored at temperatures ranging from 80 to 120°C for times spanning 1 to 30 days, depending on temperature. After aging, the nitrate ester ($-\text{ONO}_2$) content and molecular weight of the NC were measured. We did not determine either weight change or gas evolution for these tests.

The NC samples were analyzed for ($-\text{ONO}_2$) by an infrared absorption method. Samples were dissolved in tetrahydrofuran (THF) and their integrated absorbance between 1600 and 1700 cm^{-1}

was compared to that of a standard calibration curve. The analysis was performed with a concentration of about 10 mg NC per ml THF using a Digilab Fourier Transform Infrared Spectrometer, model FTS-20C, with a 0.1 cm CaF_2 cell. The error in the determination was better than $\pm 3\%$ and the precision of duplicates was $\pm 1\%$.

The molecular weight (styrene equivalent) of the NC was measured using gel permeation chromatography on the THF solutions. This technique was described in some detail in a previous report.¹ Changes in molecular weight of $\pm 5\%$ could be detected by this method.

NITRATE ESTER DECOMPOSITION

The data from the aging test are given in Table 1 for both NC and PBX-9404. The nitrate ester content is given as X, the mean ester number per NC monomer unit. The starting material is listed as "control." The value of X for NC and as-formulated PBX-9404 was the same, but the control condition for the PBX-9404 used in our studies involved a hot-pressing cycle that caused some changes in the NC. The after-pressing NC properties are listed as PBX-9404 controls.

We have already shown² that the loss of (-ONO₂) from NC in PBX-9404 is well described by the rate expression for a reaction of the type

namely,

$$k_2 t = \frac{1}{C(0)} \left[\frac{C(0) - C(t)}{C(t)} \right] \quad (1)$$

Here, k_2 is the second-order rate constant, $C(0)$ is the initial concentration, and $C(t)$ is the concentration after time, t . We have fitted our data to Eq. (1) using the same least-squares method that we used before for PBX-9404.² Here we used X as concentration. The resulting values for the second-order rate constant as a function of temperature for both PBX-9404 and for NC are given in Table 2. Since $k_2(T)$ is expected to have the form of an Arrhenius equation, we then least-squares

TABLE 1. Molecular weight and nitrate ester content of NC after thermal aging. (Dashes indicate data not obtained.)

T (°C)	t (days)	X (mean ester no.)		$\bar{M}_n$ (number-averaged molecular weight)		MWD (molecular weight dispersity)	
		PBX-9404	NC	PBX-9404	NC	PBX-9404	NC
	Control	2.27	2.31	5 700	13 100	2.79	2.75
50	243	2.16	—	4 200	—	2.36	—
	488	—	—	3 600	—	2.28	—
60	61	2.16	—	4 100	—	2.44	—
	243	2.07	—	3 400	—	2.06	—
	488	1.82	—	2 700	—	1.96	—
80	20	—	2.31 ^a	—	11 900	—	2.64
	28	2.02	—	3 300	—	2.09	—
	30	—	2.29	—	10 900	—	2.63
	59	1.89	—	2 700	—	1.89	—
	84.3	1.70	—	2 600	—	1.81	—
	89 ^b	1.81	—	2 500	—	1.88	—
	91 ^b	1.63	—	1 600	—	1.50	—
90	5	—	2.31 ^a	—	13 000	—	2.48
	10	—	2.29	—	12 400	—	2.48
	20	—	2.25	—	10 700	—	2.47
100	2	—	2.30	—	12 500	—	2.74
	5	—	2.28	—	10 500	—	2.83
	10	—	2.20	—	9 300	—	2.87
	14.2	1.82	—	2 200	—	1.73	—
120	1	—	2.18	—	10 100	—	2.71
	2	—	2.00	—	5 500	—	2.76
	3	—	1.89	—	4 300	—	3.05

^aEstimated, because our method was not sensitive enough to detect the change in the ester content.

^bThese samples had begun accelerated decomposition^{1,2} and were not included in the data treatment.

TABLE 2. Rate constants for decomposition of PBX-9404 and NC. (Dashes indicate data not obtained.)

T (°C)	$k_2(T)$ (nitrate ester loss)		$k_1(T)$ (molecular weight degradation)	
	PBX-9404	NC	PBX-9404	NC
50	$9.1 \times 10^{-5}^a$	—	2.1×10^{-7}	—
60	2.1×10^{-4}	—	3.7×10^{-7}	—
80	1.7×10^{-3}	$1.3 \times 10^{-4}^a$	2.5×10^{-6}	4.8×10^{-7}
90	—	5.8×10^{-4}	—	8.9×10^{-7}
100	$7.7 \times 10^{-3}^a$	2.2×10^{-3}	2.0×10^{-5}	3.5×10^{-6}
120	—	3.1×10^{-2}	—	5.5×10^{-5}

^aOnly a single datum was available, obviating a least-squares fit.

fitted the values of $\ln k_2$ vs $1/T$ and determined that

$$k_2(T) = 4.1 \times 10^{10} e^{-21700/RT} \quad (r^2 > 0.99),$$

for PBX-9404 (50–100°C)

$$k_2(T) = 2.6 \times 10^{19} e^{-37700/RT} \quad (r^2 > 0.99),$$

for NC (80–120°C).

The fits are very good and the difference in activation energies is consistent with a change in decomposition mechanism observed between 80 and 100°C.⁴ The values are in general agreement with those reported in the literature¹⁻¹⁰ in the same temperature regimes.

DEGRADATION IN MOLECULAR WEIGHT

The degradation in molecular weight of cellulose has been described by the random chain-scission model which assumes a first-order mechanism.¹¹ This model has recently been applied at this laboratory to a number of other plastic-bonded high explosives.¹² The molecular weight is given by the equation

$$\frac{1}{\overline{M}_n(t)} = \frac{1}{\overline{M}_n(0)} + k_1 t \quad (2)$$

where $\overline{M}_n(t)$ is the number-averaged molecular weight at time t , $\overline{M}_n(0)$ is the initial number-averaged molecular weight, and k_1 is the first-order rate constant, also assumed to have the Arrhenius form. Figures 1 and 2, for PBX-9404 and NC, respectively, show that our data can be

described by Eq. (2). The slope of the least-squares straight line fitted to the data at each temperature determines $k_1(T)$. The results are given in Table 2 for PBX-9404 and NC. Here, too, a least-squares straight line was fitted to $\ln k_1$ versus $(1/T)$; the resulting expressions were

$$k_1(T) = 3.7 \times 10^9 e^{-24400/RT} \quad (r^2 > 0.99),$$

for PBX-9404 (60–100°C),

$$k_1(T) = 3.1 \times 10^{17} e^{-39100/RT} \quad (r^2 > 0.99),$$

for NC (90–120°C).

The fit is excellent and the activation energies are close to those derived from the $(-\text{ONO}_2)$ data.

FIG. 1. Degradation of molecular weight of NC in PBX-9404 as a function of time at several temperatures. Linear relations agree with the random chain-scission model.

FIG. 2. Degradation of molecular weight of NC alone as a function of time at several temperatures. Linear relations agree with the random chain-scission model.

DISCUSSION

Given the basic premise that decomposition of nitrate ester and degradation in molecular weight are directly related, we would expect that both processes would be governed by the same activation energy, even though the processes are described by different mechanisms. This has been demonstrated in our results. An Arrhenius plot of the rate constants is shown in Fig. 3, in accordance with the least-squares fits discussed in previous sections. As mentioned, the slopes are in good correspondence; however, one difference should be noted. The decomposition rate for NC in PBX-9404 as compared to that for NC in the temperature region of overlap (80–100°C) is higher by a factor of 5–10. This difference has been seen by others,⁴ and is attributable to the effects of the other constituents of PBX-9404. In particular, PBX-9404 contains ~0.1 wt% diphenylamine¹³ as a scavenger for NO_2 . This material is a Lewis base and is expected to catalyze nitrate ester decomposition.¹⁴

If we combine Eqs. (1) and (2), we get a correlation between nitrate ester concentration and molecular weight of NC that can be used as a predictive expression. This way of being able to predict nitrate ester concentration is valuable, because determination of nitrate ester concentration in

FIG. 3. Arrhenius plot of rate constant vs $(1/T)$ for degradation of NC alone and NC in PBX-9404. The open symbols are for second-order nitrate ester decomposition, and the full symbols are for first-order molecular weight degradation. The circles are for NC in PBX-9404, and the triangles for NC alone.

PBX-9404 is complicated and subject to large errors due to interference from HMX, RDX, nitrated DPA products, etc. The correlation is given by Eq. (3):

$$\frac{1}{\bar{M}_n(0)} \left[\frac{\bar{M}_n(0)}{\bar{M}_n(t)} - 1 \right] = \frac{A_2}{A_1} \left[\frac{1}{C(0)} \right] \left[\frac{C(0)}{C(t)} - 1 \right] \quad (3)$$

The terms A_1 and A_2 are the pre-exponential factors in the first- and second-order rate expressions, respectively. When the left hand quantity of Eq. (3) is plotted versus the right hand variable, we expect a straight line with slope A_2/A_1 . This plot is shown in Fig. 4 and the associated terms of Eq. (3) are given in Table 3. A least-squares straight-line was fitted to the data. The slope (indicating the value of A_2/A_1) was 1.8×10^{-3} , with $r^2 = 0.87$.*

A linear fit does not weight many of the NC data points because they fall close to the origin, so we also tried a least-squares fit to the power expression

$$\frac{1}{\bar{M}_n(0)} \left[\frac{\bar{M}_n(0)}{\bar{M}_n(t)} - 1 \right] = B \left\{ \left[\frac{1}{C(0)} \right] \left[\frac{C(0)}{C(t)} - 1 \right] \right\}^n$$

The fit gave $n = 0.96$ and $B = 1.8 \times 10^{-3}$, with $r^2 = 0.91$. This is essentially equivalent to the fit with Eq. (3), which we will assume to be correct.

We observed another difference in behavior between NC in PBX-9404 and pure NC, namely, that the molecular weight dispersities were very different after degradation. We have plotted the molecular weight dispersity (MWD) as a function of $\bar{M}_n(t)$ in Fig. 5. (The molecular weight dispersity is defined as $MWD = (\bar{M}_w)/(\bar{M}_n)$, where $\bar{M}_w$ is the weight-averaged molecular weight.) For

FIG. 4. Nitrate ester decomposition and molecular weight degradation. Circles are for NC in PBX-9404; the triangles are for NC alone.

NC, MWD remains essentially constant throughout the process, while for PBX-9404, MWD decreases linearly with $\bar{M}_n$ and approaches a monodisperse state for total degradation ($\bar{M}_n(t) \rightarrow 0$). The significance of this finding is not obvious, but it certainly reflects the effects of the other ingredients of PBX-9404 on the NC decomposition process.

Observations in our previous study have led us to suggest that in the course of NC decomposition in PBX-9404 the tri-esterified NC units decompose first.² However, Volltrauer and Fontijn⁴ interpreted their results as indicating that diesters were the first to decompose. We have re-examined our data and want to present another argument that the triesters are the first to disappear.

Several possible distributions of fully and partially esterified cellulose units yielding a cellulose nitrate with $X = 2.31$ were calculated using a Monte Carlo method.² Of these, the one that best conforms to our results was one in which mono-, di-, and tri-esters were allowed, but no unesterified units were allowed. The results of that calculation are summarized in Table 4. Given the analyses in Ref. 2 for nitrate ester content, NC content and fractional decomposition of $(-ONO_2)$ and NC, we can calculate the mean ester number of the residual and the decomposed NC. These values are plotted in Fig. 6. The full symbols represent

*The intercept was 1.1×10^{-5} .

TABLE 3. Calculated values for Eqs. (1) and (2). (Dashes indicate data not obtained.)

T (°C)	t (days)	$\frac{1}{\bar{M}_n(0)} \left[\frac{\bar{M}_n(0)}{\bar{M}_n(t)} - 1 \right]^*$		$\frac{1}{C(0)} \left[\frac{C(0)}{C(t)} - 1 \right]^\dagger$	
		PBX-9404	NC	PBX-9404	NC
50	243	6.3×10^{-5}	—	0.022	—
	488	1.0×10^{-4}	—	—	—
60	61	6.9×10^{-5}	—	0.022	—
	243	1.2×10^{-4}	—	0.043	—
	488	2.0×10^{-4}	—	0.11	—
80	20	—	7.7×10^{-6}	—	$\leq 0.001^a$
	28	1.3×10^{-4}	—	0.055	—
	30	—	1.5×10^{-5}	—	0.0038
	59	2.0×10^{-4}	—	0.089	—
	84.3	2.1×10^{-4}	—	0.15	—
	89 ^b	2.2×10^{-4}	—	0.11	—
	91 ^b	4.5×10^{-4}	—	0.17	—
90	5	—	3.1×10^{-7}	—	$\leq 0.001^a$
	10	—	4.4×10^{-6}	—	0.0038
	20	—	1.7×10^{-5}	—	0.012
100	2	—	3.7×10^{-6}	—	0.0019
	5	—	1.9×10^{-5}	—	0.0057
	10	—	3.3×10^{-5}	—	0.022
	14.2	2.8×10^{-4}	—	0.11	—
120	1	—	2.2×10^{-5}	—	0.026
	2	—	9.0×10^{-5}	—	0.050
	3	—	1.6×10^{-4}	—	0.096

*Molecular weight degradation.

†Nitrate ester loss.

^aEstimated, because our method was not sensitive enough to detect the change in the ester content.

^bThese samples had begun accelerated decomposition^{1,2} and were not included in the data analyses.

decomposed NC and the open symbols are for the residual NC. The solid curves are calculated on the following assumptions: the mean ester number (X) starts at 2.31; the NC subunit population is that shown in Table 4; at first triesters disappear exclusively; when the triesters are gone, the remaining NC, consisting of mono- and di-esters only, decomposes congruently. It is evident that this simple picture is in good agreement with observations.

TABLE 4. Result of the Monte Carlo calculation for population of esterified subunits in NC with X = 2.31.

NC subunit	Mole fraction
Non-esterified	0
Monoesters	0.186
Dieters	0.318
Triesters	0.496

FIG. 5. Molecular weight dispersity and number-averaged molecular weight. Circles are for NC in PBX-9404; the triangles are for NC alone.

FIG. 6. Residual NC in PBX-9404 (open circles) and decomposed NC (full circles) as a function of fractional loss of nitrate ester. The lines represent a model that assumes that triesterified NC subunits decompose first.

CONCLUSIONS

The kinetics of decomposition of NC, both "pure" and in PBX-9404, are shown to be consistent with (a) the simple first-order model of random chain-scission with respect to molecular weight degradation, and (b) a second-order nitrate ester decomposition. We also found that the activation energies characterizing the processes between 50 and 120°C are in agreement with available values in the literature. A change in the decomposition process is seen between 80 and 100°C. A correlation has been calculated between

molecular weight and nitrate ester content of NC that can be used predictively. It has been confirmed that, at a given temperature, decomposition of NC in PBX-9404 is faster than undiluted NC. The polydispersity of NC after decomposition remains constant for NC alone while it becomes more narrow for NC in PBX-9404. Finally, additional calculations indicate that for NC decomposition in PBX-9404 the triesterified subunits decompose first.

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