# Low Temperature Non-Isothermal Aging of Nitrocellulose

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### Abstract

Slow multi-sample thermal ramp aging experiments were performed on high viscosity lacquer grade nitrocellulose over the temperature range 30-80°C. Nitrocellulose was used in the fibrous state, in solution and as the gelatinous nitro-plasticized binder used to bind high explosive crystals (HMX) in a polymerbonded explosive (PBX) formulation. Samples were subjected to a slow, stable heating rate (dT/dt) of 10 °C per day with periodic sample withdrawal for analysis by triple detector size exclusion chromatography (SEC). Molecular weight and intrinsic viscosity data indicate inter-chain recombination/aggregation for fibrous material or highly concentrated solutions, when dry. When in fibrous or gelatinous binder form, little degradation was observed, aside from apparent recombination/aggregation. As a concentrated solution complex behavior was noted; fast eluting peaks formed with increased temperature, accompanied by rapid molecular weight reduction and a marked decrease in light scattering peak area. Progressive dilution of nitrocellulose solutions and/or addition of very small quantities of water reduced the recombination/aggregation effects but did not appear to significantly affect the overall rate of nitrocellulose degradation. Activation energies for nitrocellulose chain scission have been estimated from the molecular weight and intrinsic viscosity data obtained by the thermal ramp method.

**Keywords:** Nitrocellulose, Molecular Weight, Size Exclusion Chromatography, Non-Isothermal Aging, Activation Energy

## **1** Introduction

Nitrocellulose, or gun cotton, is derived from cellulose, a naturally abundant high-molecular-weight polysaccharide of  $\beta$ -1,4-anhydroglucose repeat units. It is widely used in protective coatings and lacquers, inks and as the major component of many single and double base propellants. Our interest in nitrocellulose relates to its use as the binder component of a polymer-bonded explosive (PBX) formulation, in which it contributes positively to mechanical and hazard properties. Clearly, physical and chemical changes in nitrocellulose that occur with age will affect both the mechanical and safety properties of the PBX making a good understanding of the degradation processes under realistic conditions essential.

Extensive low temperature PBX isothermal accelerated aging experiments were performed to investigate the effects on nitrocellulose molecular weight [1]. In these experiments, a range of temperatures significantly above ambient were employed ( $\sim 30-70^{\circ}$ C) to isothermally incubate samples for extended time periods in order to determine reliable kinetic parameters (e.g. activation energy,  $E_a$ , Arrhenuis pre-exponential, A). A robust experimental method that could achieve these kinetic parameters in a greatly reduced timescale would therefore be highly desirable.

Qualitative slow thermal ramp methods were used by Camino et al. [2] to investigate thermal aging of cellulose in the form of Kraft paper. The technique was further developed by Emsley and Heywood [3] with the development of a rigorous kinetic model describing the degradation of cellulose in terms of degree of polymerization (DP). The study reported herein applied the same thermal ramp methods to nitrocellulose with a view to proving its applicability as a technique for rapidly monitoring and investigating aging characteristics from which Arrhenius parameters may be derived. Furthermore, the thermal ramp technique lends itself to the rapid assessment of the effects of environment on the stability of nitrocellulose.

# 2 Experimental

Pristine cotton linter-derived nitrocellulose (11.7-12.2%) nitrogen) was used in the preparation of samples for the multi-sample slow thermal ramp experiments. For experiments on solids, 5 mg samples of nitrocellulose were weighed into 2 cm<sup>3</sup> glass GPC vials and securely crimp-sealed with the appropriate aluminum/rubber caps. Nitrocellulose solutions were prepared as bulk solutions of varying concentrations (7.5, 15, 30 and 60 mg cm<sup>-3</sup>) in A. R. grade dimethylsulphoxide (DMSO) and a 0.5 cm<sup>3</sup> aliquot decanted into 2 cm<sup>3</sup> GPC vials, which were also sealed. DMSO was selected for reasons of good solubility and for its high boiling point and was used without further purification other than drying over a 0.4 nm molecular sieve.

The thermal ramp apparatus comprised a cylindrical brass heating block (with close-fitting machined brass lid) sur-

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rounded by a heating jacket. An RKC REX-P300 programmable controller provided highly stable temperature control and temperature ramp rates. The 2 cm<sup>3</sup> GPC sample vials (up to 15) were placed in the heating block and heated together at a ramp rate of 10 °C per day. Samples were removed from the heating block at regular intervals over the temperature profile of the 30-75 °C ramps.

On removal from the ramp apparatus samples were stored at ambient temperature prior to preparation for SEC analysis. The sample vials were then opened and the contents diluted with 1 cm<sup>3</sup> of stabilized HPLC grade tetrahydrofuran (THF). The resealed sample vials were stored at ambient temperature for a period of 7 days to allow for full dissolution of the nitrocellulose into the THF: it has been shown that stable molecular weight measurement by SEC is only possible when dissolution of the nitrocellulose has stabilized [1].

SEC analysis was performed using a Viscotek triple detector system comprising a Model 250 combined refractive index and viscometry detector and a Model 600 right angle laser light scattering (RALLS) detector. The mobile phase was HPLC grade tetrahydrofuran (stabilized with 100 ppm butylhydroxytoluene) and the columns ( $2 \times 30$  cm length) were packed with 10 µm PLGel<sup>TM</sup> Mixed-B cross-linked polystyrene. Subsequent data acquisition and analysis was facilitated by Viscotek Trisec<sup>3</sup> software [4].

Weight average molecular weight  $(M_w)$  and intrinsic viscosity  $(\eta_w)$  data were plotted against temperature and fitted, assuming degradation obeys the simple relationship used by Ekenstam [5] (Eq. (1)). Data analysis and Arrhenius parameterization were facilitated by the use of the commercial 'ModelMaker' modeling program [6] to solve the differential equations according to the rationale presented by Heywood et al. [7].

# **3** Results and Discussion

Thermal ramp experiments have been performed on dry fibrous nitrocellulose, as a solution in dimethylsulphoxide

(DMSO) over a wide range of concentrations, as a gelatinous binder plasticized with the nitro-aromatic liquid, K10 (a eutectic mixture of nitroethylbenzenes), and as a solution of binder in DMSO. Right angle laser light scattering (RALLS) SEC data are presented in Figure 1 for the fibrous nitrocellulose. These data demonstrate that the behavior of nitrocellulose in this state is complex. What would appear to be a high mass peak is present throughout the thermal ramp, offering evidence for association of nitrocellulose chains into high hydrodynamic volume species. Regardless of their origin such chromatographic features make it very difficult to reliably determine average molecular weight values (e. g.  $M_n, M_w$ ) with certainty. Aside from apparent association, there is little or no observable degradation of the nitrocellulose as a result of the applied thermal ramp  $(30-80^{\circ}C)$ .

When in DMSO solutions there are pronounced aging effects during the thermal ramp experiment. At the highest nitrocellulose concentration (i.e.  $60 \text{ mg cm}^{-3}$ ), RALLS data (presented in Figure 2) betrays evidence of very complex behavior of the aged samples, far more so than for the fibrous samples. As temperature increases, the main chromatographic peak shifts toward greater retention volume (i.e. lower molecular weight) and there is evidence for the formation of new rapidly eluting peaks as the temperature is increased to ~ $60 \,^{\circ}$ C. As temperature is further increased, the process appears to involve all peaks shifting to longer retention volume with no loss of observed chromatographic complexity.

This complex behavior is indicative of high size species possibly caused by: (*i*) formation of nitrocellulose moieties of greater molecular mass than the starting material through aggregation or chemical recombination, (*ii*) a significant change in conformational behavior of individual polymer chains which significantly increases their hydrodynamic volume. At present we have no information to confirm one particular hypothesis, but what is clear is that the 60 mg cm<sup>-3</sup> concentration data would not provide robust molecular weight ( $M_w$ ) or intrinsic viscosity values ( $\eta_w$ ) suitable for calculating Arrhenius kinetic parameters for nitrocellulose



Figure 1. SEC-RALLS chromatograms for fibrous nitrocellulose

Propellants, Explosives, Pyrotechnics 30 (2005), No. 3



Figure 2. SEC-RALLS chromatograms for nitrocellulose degradation as a 60 mg cm<sup>-3</sup> solution in DMSO

degradation. It is noteworthy that the fast eluting species, witnessed only by the RALLS detector, exist in very low concentrations, suggesting that they must have very high light scattering efficiency. The differential molecular weight distributions show no evidence for the presence of significant high mass species. These observations further support the existence of complex aggregates in solution.

To test the aggregation theory successive dilutions of the  $60 \text{ mg cm}^{-3}$  solution were performed. In line with our expectations chromatographic complexity was reduced markedly as nitrocellulose concentration was reduced. The RALLS data for the most dilute solution (i.e. 7.5 mg cm<sup>-3</sup>), presented in Figure 3, is very much simplified and supports our expectation that the tendency for intermolecular association would be dependent on chain proximity and hence concentration. As temperature increases, the position of the RALLS peak shifts toward greater retention volume with no evidence for the complexity of behavior noted above at lower temperatures. The dilute solution data offer

the best opportunity to obtain kinetic parameters (e. g. activation energy) for degradation of nitrocellulose under conditions in which chain scission predominates.

It is noteworthy that there is a significant build-up of slow eluting (~19 minutes) low molecular weight species as the temperature increases and degradation proceeds. This was unexpected as these species must have molecular weights in a region where RALLS sensitivity is very much reduced. This narrow peak indicates that either (*i*) a very large concentration of consistently small chain species are being produced as a result of scission or (*ii*) a range of small species are being generated but the peak returns to baseline due to lack of RALLS sensitivity rather than lack of eluting material. If a consistently small molecular weight species is produced, its molecular weight can be no greater than 200– 500 Dalton (1 Dalton = 1 u = 1 atomic mass unit) which would indicate that the degradation products are monomeric and dimeric chain fragments.



Figure 3. SEC-RALLS chromatograms for nitrocellulose degradation as a 7.5 mg cm<sup>-3</sup> solution in DMSO

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Propellants, Explosives, Pyrotechnics 30 (2005), No.3

Cellulose degradation is thought to occur via non-random mechanisms in which polymer chains preferentially break either near their centers or close to the end of a chain [8, 9]. The latter would result in production of a high concentration of very low molecular weight species and reduction in the molecular weight of the bulk. The thermal ramp experiments show similar trends with rapid production of very low molecular weight species, and the slow shift of the main nitrocellulose peak towards reduced molecular weight. This would suggest that the predominant aging mechanism is one where non-random chain scission occurs a short distance from the ends of nitrocellulose polymer chains.

As the gelatinous nitro-plasticized binder, aging effects are minimal, much like the fibrous nitrocellulose. However, as a DMSO solution (nitrocellulose at 7.5 mg cm<sup>-3</sup>) binder aging effects are straightforward and pronounced. These observations closely mirror the situation with unplasticized nitrocellulose, indicating that the presence of K10 has little effect on the degradation of nitrocellulose in these experiments.

For the 7.5 mg cm<sup>-3</sup> nitrocellulose solution data, the consistency of the calculated  $M_w$  and  $\eta_w$  values is apparent when plotted against the ramp temperature, as illustrated in Figures 4 and 5. Very little scatter is observed in the data sets, allowing for robust curve fitting to be undertaken. The quality of this data confirms the reproducibility of our SEC



**Figure 4.** The change in molecular weight with temperature for a  $7.5 \text{ mg cm}^{-3}$  nitrocellulose solution in DMSO



**Figure 5.** The change in intrinsic viscosity with temperature for a  $7.5 \text{ mg cm}^{-3}$  nitrocellulose solution in DMSO

Propellants, Explosives, Pyrotechnics 30 (2005), No. 3

technique as applied to nitrocellulose analysis. Comparison with the plots derived from the binder experiments (Figures 6 and 7) shows strong similarities in terms of scatter and consistency. (The single erroneous data point in Figure 6 ( $\sim$  323 K) is thought to be due to SEC instrumental issues).

#### 3.1 Kinetic Modeling of Experimental Data

The kinetic method used to describe the thermal ramp degradation of cellulose [3, 7] was taken as a starting point for the degradation kinetics of nitrocellulose in solution, but using the equation used by Ekenstam [5] rewritten in terms of  $M_w$  or  $\eta_w$  (e.g. Eq. 1) as the basis of the model.

$$\frac{1}{M_w(t)} = \frac{1}{M_w(0)} + kt \tag{1}$$

The rate of change of the rate constant, k, with respect to temperature, is calculated by differentiating the Arrhenius equation with respect to temperature which yields the following differential equation (Eq. (2)):

$$\frac{dk}{dT} = -\frac{E}{RT^2} \cdot Ae^{\frac{-E}{RT}} = -\frac{E}{RT^2} \cdot k$$
(2)



**Figure 6.** The change in molecular weight with temperature for a solution of binder in DMSO (nitrocellulose at 7.5 mg cm<sup>-3</sup>)



**Figure 7.** The change in intrinsic viscosity with temperature for a solution of binder (nitrocellulose at 7.5 mg cm<sup>-3</sup>) in DMSO

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Low Temperature Non-Isothermal Aging of Nitrocellulose

If molecular weight is plotted against absolute temperature, it is assumed that

$$\frac{dT}{dt} = 1$$

'ModelMaker' software [6] was used to empirically fit the data to simultaneously solve Eq. (2) and the differential form of Eq. (1), differentiated with respect to temperature (Eq. (3)).

$$\frac{dM_w}{dT} = \frac{dM_w}{dt} \cdot \frac{dt}{dT} = -k \cdot M_w^2 \tag{3}$$

The fitted curves of both  $M_w$  and  $\eta_w$  data for the 7.5 mg  $cm^{-3}$  nitrocellulose sample (Figures 4, 5) and the binder in solution (Figures 6, 7), take the form of a reverse sigmoid with two points of inflexion over the applied thermal ramp. The kinetic parameters resulting from curve fitting (Table 1) are extremely sensitive to small changes in the underlying experimental data. It is critically important to obtain sufficient data to adequately describe (i) the initial starting value, (ii) the inflexion where the data turn down at 37- $47 \degree C (310-320 \text{ K})$ , and (*iii*) the inflexion where the data begin to flatten out at 67-77 °C (340-350 K). In this respect limitations are imposed by the sample capacity of the ramp apparatus and safe working conditions. Experiments have been repeated with sets of fifteen individual samples; different withdrawal temperatures were sampled on each ramp run to give even coverage and withdrawals were concentrated at temperatures of greatest  $M_{w}$  or  $\eta_{w}$  gradient change. This approach was employed for the nitrocellulose and binder where two replicate ramp experiments were performed on each sample (sampled from a stock solution of each), and data combined and treated as though from a single experiment. This approach has illustrated the reproducibility of the thermal ramp technique and the SEC analysis and shown that, time permitting, any number of carefully controlled experiments could be performed and combined to give as complete a data set as required. Since each experiment only takes approximately five days this is feasible, as shown by the data in Figure 7 in particular. Any disparity in the activation energy values obtained in these experiments on low concentration DMSO solutions of nitrocellulose  $(137-157 \text{ kJ mol}^{-1})$  and solutions of binder  $(120-165 \text{ kJ mol}^{-1})$  reflect the subtle differences between molecular weight and intrinsic viscosity as actual measurement techniques rather than analytical error.

Estimates of activation energy can be used to provide an assessment of the most likely mechanism of nitrocellulose degradation in these experiments. Table 2 lists reported experimental activation energies for the degradation of nitrocellulose over a temperature range broadly comparable to that employed in the thermal ramp experiments [10]. Of particular note, the activation energy for nitrocellulose molecular weight degradation in a PBX formulation subjected to conventional long-term isothermal aging (135 kJ  $mol^{-1}$ ) is in good agreement with the results of our thermal ramp experiments. Also, activation energy of 179 kJ mol<sup>-1</sup> has been reported for nitrocellulose molecular weight reduction as a result of non-isothermal aging techniques [11]. This non-isothermal work suggested that evolution of  $NO_x$  was the rate determining step which then led to the scission of one chain segment.

The range of experimental activation energy values compares well with accepted literature values (~ 160 kJ mol<sup>-1</sup>) reported for thermolytic scission of nitrocellulose with associated evolution of NO<sub>x</sub> [12]. It is however by no means certain that thermolytic degradation is the only degradation mechanism as it is likely that residual moisture in the system will be present in sufficient quantity to promote and sustain acid-catalyzed hydrolytic chain scission

Table 1. Arrhenius kinetic parameters from thermal ramp experiments

Parameter, Sample	$E_a (kJmol^{-1})$	А
$\overline{M_{\rm wp}}$ nitrocellulose (7.5 mg cm <sup>-3</sup> in DMSO)	137	$2.51 \times 10^{15} \text{ Dalton}^{-1}$
$M_{\rm w}$ binder (7.5 mg cm <sup>-3</sup> in DMSO)	120	$3.02 \times 10^{12} \text{ Dalton}^{-1}$
$\eta_{w}$ , nitrocellulose (7.5 mg cm <sup>-3</sup> in DMSO)	157	$1.20 \times 10^{23} \text{ dl g}^{-1}$
$\eta_{\rm w}$ , binder (7.5 mg cm <sup>-3</sup> in DMSO)	165	$1.16 \times 10^{23} \text{ dl g}^{-1}$

Table 2.	Reported	Arrhenius	kinetic	parameters	for	degradation	over the	e tem	perature	range	0 - 200	)°(
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Activation Energy kJ mol <sup>-1</sup>	<sup>°</sup> C	Sample/Technique	Reference	
156	30-80	Reported herein	this work	Chain Properties
221	70-90	NC/SEC	[10]	-
179	0 - 200	NC/Weight loss	[10]	
135	34-66	PBX/SEC	[1]	
106	25-77	$NO_x$ chemiluminescence	[10]	Gaseous Products
111	50 - 100	Evolved gases	[10]	
58	40-90	O <sub>2</sub> /C=O chemiluminescence	[10]	

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Propellants, Explosives, Pyrotechnics 30 (2005), No.3

reactions. This is particularly likely if acidic  $NO_x$  species are formed within the closed environment of a sealed vial.

The purpose of accelerated aging experiments is to provide information related to the real time low temperature aging of the material under investigation. It is possible to estimate how the values of  $M_w$  and  $\eta_w$  at the end of the thermal ramp experiment equate to isothermal aging experiments at a given low temperature (e. g.  $30^{\circ}$ C). The simplest possible approach is to assume the same mechanism of degradation for both thermal ramp and isothermal degradation and calculate an instantaneous rate constant, k, at 30°C on the thermal ramp profile. This allows an isothermal plot of  $M_w$  and  $\eta_w$  vs. time to be constructed according to Eq. (1), from which the comparable level of isothermal degradation can be determined. This approach leads to the assertion that the degradation achieved at the end of the thermal ramp experiment is equivalent to approximately 11 years at 30°C. However, this is only the case for lacquer grade nitrocellulose in DMSO solution at the given concentration of 7.5 mg  $cm^{-3}$ . Isothermal data is not yet available for this particular experimental configuration and so it should be treated as an illustration that thermal ramp analysis can be related to real time aging.

# 4 Conclusions

This work has established thermal ramp analysis as a viable and successful method of accelerating the aging of nitrocellulose and a nitro-plasticized nitrocellulose binder formulation. Activation energies have been calculated in a very short timescale and the values obtained (120-165 kJ mol<sup>-1</sup>) compare favorably with those derived from conventional isothermal aging experiments ( $135 \text{ kJ mol}^{-1}$ ). If precautions are taken to control thermal ramp rate very accurately, the experimental procedure is simple and rapid such that Arrhenius parameterization can be performed in a matter of days. In combination with SEC analysis, the technique has been shown to be highly reproducible and offers the potential for rapid investigation of environmental factors influential to aging of nitrocellulose. The experiments described herein will be extended to the full PBX formulation under a range of credible storage conditions in an attempt to better understand the role of relative humidity and the presence of oxygen on long-term chemical stability. Studies on the degradation of cellulose have indicated that oxidation reactions can lead to chain scission and reduction in molecular weight. [13, 14] It is expected that nitrocellulose will undergo similar degradation chemistry in which the presence of oxygen at elevated temperature has been shown to exhibit a synergistic aging effect.

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