

Chapter 2

Nitration and Denitration Sequence of Nitrocellulose

[Added as preamble for Chapter 4 below]

[Review usage of NO_x for consistency with the whole text. Maybe just stick to "nitrous oxides" for the whole document.]

2.1 Introduction

Moniruzzaman *et al.* used the **UV!** absorption of an anthraquinone dye to determine the activation energies for the removal of the nitrate at C2, C3, C6 sites on **NC!** (**NC!**) (figure 2.1)[?, ?]. **UVVis!** was chosen as an efficient, non-destructive method of monitoring the decomposition process. The reaction of the **SB59!** (**SB59!**) with NO_x released by denitration, mimics the action of stabilisers such as **DPA!** (**DPA!**) and **2NDPA!** (**2NDPA!**) commonly used in **NC!** formulations. The secondary amine groups of the dye consume any nitrates in the system, eliminating the possibility of successive reactions generating acidic species. The presence of acid has been linked to autocatalytic rates of degradation during later stages of **NC!** degradation[?, ?, ?, ?].

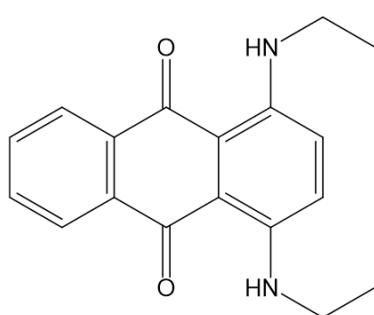


Figure 2.1: **SB59!** (**SB59!**) used to probe the release of nitrates from **NC!** using **UVVis!** (**UVVis!**) and ^1H NMR spectroscopy[?].

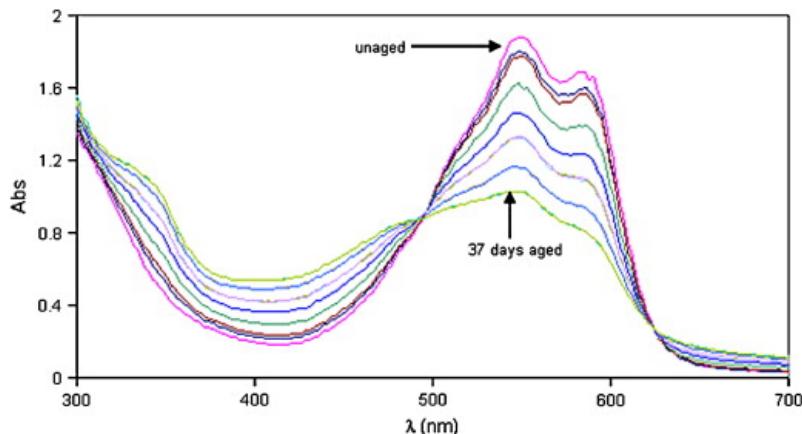


Figure 2.2: UV-vis spectra of NC! thin films with and without accelerated ageing at 60 °C, over a total time of 37 days, from the work of Moniruzzaman *et al.*[?]. The unaged peak demonstrates a strong absorbance in the region corresponding to the SB59! dye (. This decreases as the dye is consumed in the reaction of NO_x released upon NC! denitration.

Decreasing absorption peak intensity of the dye and appearance of new absorption regions gave insight into the extent of denitration and the presence of secondary reaction products (figure 2.2). The NC! starting material was 12.15%N by mass, with mean DOS! (**DOS!**)=2.307, indicating that individual glucopyranose rings were of mixed nitration level with non-uniform distribution of nitrate groups along the polymer. The study found that the nitrate at the C3 position would be most reactive, possessing the lowest activation barrier to removal. This was followed by C2 and C6. The findings contrast with the computational work of Shukla *et al.*, who determined that denitration via alkylaline hydrolysis followed the order of C3→C6→C2 [?, ?]. In this case, the study only considered the fully nitrated system. There is evidence that nitration and denitration are influenced by the presence of nitrate groups at adjacent positions. Matveev *et al.* demonstrated that for polynitro esters the rate of liquid-phase decomposition did not increase linearly with number of nitrate reaction centres, but was mainly dependent on individual structures table 2.1[?]. It was suggested that the trend in reactivity could be explained by the inductive effect of nitrate groups [?]. Hu *et al.* found that the presence of adjacent OH groups hampered the rate of hydrolysis for aerosol dispersed organonitrates [?]. It is therefore ambiguous whether the apparent rate increase due to adjacent nitrate groups arises as a result of the inductive effect of the nitrate, or whether it is solely due to the absence of the neighbouring hydroxyl.

The inductive effect arises when a difference in the electronegativity between atoms connected by a σ bond leads to a polarisation, or permanent dipole, in the bond. Electron donating groups increase the $\delta-$ partial charge on neighbouring atoms through the release of

Table 2.1: Comparison of rate constants of decomposition for various polynitrate esters at 140°C. Collated from literature sources by Matveev *et al.*[?].

Compound	ΔT / °C	E / kcal mol ⁻¹	$\log A$ [s ⁻¹]	k_{expt} / 10 ⁻⁶ s ⁻¹
O ₂ NOCH ₂ CH ₂ CH ₂ ONO ₂	72–140	39.1	14.9	1.7
O ₂ NOCH ₂ CH ₂ CH ₂ CH ₂ ONO ₂	100–140	39.0	14.7	1.1
O ₂ NOCH(CH ₃)CH(CH ₃)ONO ₂	72–140	40.3	14.9	5.0
O ₂ NOCH ₂ CH ₂ OCH ₂ CH ₂ ONO ₂	80–140	42.0	16.5	1.9
O ₂ NOCH ₂ CH(OH)(CH ₂ ONO ₂)	80–140	42.4	16.8	2.3
O ₂ NOCH ₂ CH(ONO ₂)(CH ₃)	72–140	40.3	15.8	3.0
[(O ₂ NOCH ₂)CH(ONO ₂)CH(ONO ₂)] ₂ (hexanitromannite)	80–140	38.0	15.9	63.0

electrons, whilst electron withdrawing groups pull electron density away from neighbouring atoms generating a $\delta+$ charge on connected atoms. From the studies above, it is seen that the denitration order of **NC!** can be influenced by the location, distribution and saturation of the nitrated sites along the polymer, as well as mechanistic differences in thermal and chemical degradation. Crucially, a synergistic effect leading to facile removal of the C3 group when the C2 site is also nitrated may play an important part in the decomposition pathway. The **DOS!** value of the source **NC!** would therefore give an indication of the likelihood of adjacent nitrates.

