

Abbreviations

| | |
|-------------------------------------|---|
| ψ | wavefunction |
| %N | percentage nitrogen by mass |
| 2-NDPA | 2-Nitrodiphenylamine |
| a.u. | atomic units |
| B3LYP | Becke, 3-parameter, Lee-Yang-Parr hybrid functional |
| BCP | bonding critical point |
| CH₃CH₃ | NC repeat unit with two –OCH ₃ capping groups |
| CH₃OH | NC repeat unit with –OCH ₃ capping group on ring 1 and –OH group on ring 2 |
| CCP | cage critical point |
| CP | critical point |
| DFT | density functional theory |
| DSC | differential scanning calorimetry |
| DOS | degree of substitution |
| DPA | diphenylamine |
| EM | energetic materials |
| EN | ethyl nitrate |
| ESP | electrostatic potential |

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|-------------------------|---|
| G09 | Gaussian 09 revision D.01 |
| GM | genetically modified |
| GView | Gauss View 5.0.8 |
| HF | Hartree Fock theory |
| IR | infra-red spectroscopy |
| MEP | minimum energy path |
| MM | molecular mechanics |
| MMFF94 | Merck molecular force field 94 |
| MP2 | Møller–Plesset perturbation theory with second order correction |
| MW | molecular weight |
| NC | nitrocellulose |
| NCP | nuclear critical point |
| NG | nitroglycerine |
| NMR | nuclear magnetic resonance spectroscopy |
| OHCH₃ | NC repeat unit with –OH capping group on ring 1 and –OCH ₃ group on ring 2 |
| PCM | polarisable continuum model |
| PES | potential energy surface |
| PETN | pentaerythritol tetranitrate |
| PETRIN | pentaerythritol trinitrate |
| QM | quantum mechanics |
| QTAIM | quantum theory of atoms in molecules |
| RCP | ring critical point |

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|----------------------------------|--|
| SB59 | 1,4-bis(ethylamino)-9,10-anthraquinone dye |
| SEM | scanning electron microscopy |
| S_N2 | bi-molecular nucleophilic substitution reaction |
| TG | thermogravimetric analysis |
| TS | transition state |
| UFF | universal force field |
| UV | ultraviolet |
| UVvis | ultraviolet-visible spectroscopy |
| ωB97X-D | ω B97X-D long-range corrected hybrid functional |
| ZPE | zero-point energy |

Chapter 1

Introduction

1.1 The modern history of Nitrocellulose

nitrocellulose (NC), cellulose nitrate, or "guncotton" is a nitrated cellulose derivative that has been widely utilised in the manufacture of plastics, inks, propellant formulations and thin films since it's discovery in 1833 by Braconnot. Cellulose is the primary component of



Figure 1.1: Comparison of degradation times for Natureflex™with conventional plastic packaging, from the Mindful Chef blog [1].

plant cell walls and is the most abundant polymer in nature [2]. Cotton is almost entirely comprised of cellulose. It can be considered an almost inexhaustible ingredient in manufacturing. As environmental concerns drive the shift towards renewable raw materials and carbon neutral industrial processes, interest and innovation in the use of bio-materials has also skyrocketed [3, 4, 5, 1]. Bio-plastic products utilising thin films made of cellulose fibres, such as Natureflex™[6], have emerged in the consumer market offering attractive replacements to traditional crude-oil plastics (figure 1.1)These alternatives provide biodegradable food packing films, 3D printing elements, wound dressings and film-blown plastics spanning almost the full range of current applications, with the added benefit of compostability, for use as a fertiliser for agricultural applications, creating a circular carbon economy [7].

It was found by Braconnot that when cellulose fibres, in the form of sawdust, cotton,

linen and paper were treated with nitric acid, the product burned rapidly and in the absence of the thick black smoke that was characteristic of gunpowder of the era [8]. In his Berlin laboratory in 1845, Dr. Schönbein serendipitously discovered that acid treated cotton wool burned violently without the accompanying black smoke that was typical of gunpowders of the time [9]. He was granted a U.S. patent the following year.

Today NC is present in adhesives, paints and lacquer coatings [10]. Varieties of high percentage nitrogen by mass (%N) are used for its explosive properties, such as in rocket and gun propellants. Since Schönbein's day NC has seen applications in dynamite, artificial silks and printing inks. Reels of historical cinematographic film were made of NC which were notoriously flammable, not premitted on public transport, and requiring storage and use only within in fire-proof projection boxes [11, 12, 13, 14]. Collodin, a solution of NC in either ether or ethanol, is used both in surgical dressings and in theatrical make-up. The non-flexible variety is applied to skin, which puckers as the solvent evaporates, effectively creating the appearance of scarred tissue.

NC of above 12.5 %N is considered explosive. The theoretical maximum level of nitration is 14.14 %N, corresponding to a degree of substitution (DOS) of three, where every free hydroxyl group has been replaced by a nitrate ester. In practice, a maximum of 13.6 %N is achieved [15]. When NC is the only energetic component in an explosive mixture, it is termed a single-base propellant. NC mixtures with one or more energetic materials (EM) such as nitroglycerine (NG), where NG also acts as a plasticiser, are classed as double or triple-base propellants. Due to the degradation of NC over time, stabilisers are necessary to neutralise the decomposition products that facilitate further reactions.

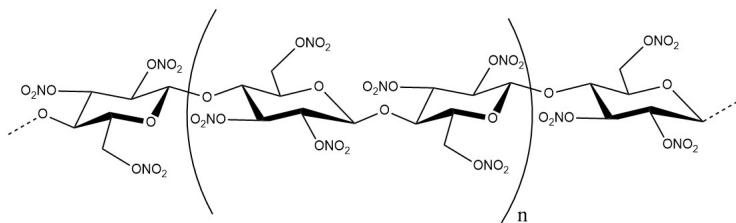


Figure 1.2: The structure of Nitrocellulose.

1.2 Synthesis and structure

Nitrocellulose is derived from the nitration of cellulose. A common nitrating mixture of nitric and sulfuric acids generate the nitronium ion (equation 1.1). The nitronium ion is

then attacked by the lone pair on the oxygen of the alcohol group on cellulose, leading to nitration (equation 1.2 and figure 1.3).



The R group here refers to the polysaccharide backbone of cellulose.

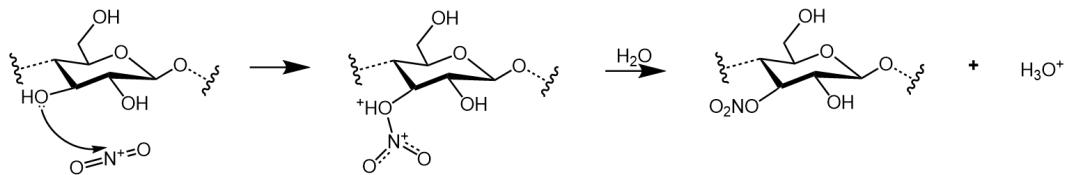


Figure 1.3: The mechanism of nitration of cellulose by nitric and sulfuric acids.

Biological variation in cellulose has implications on the quality and properties of the NC produced. During synthesis, the backbone of cellulose is largely preserved [16, 17]. Wood pulp and cotton linters are two major sources of starting material for NC production; though more expensive, cotton linters are preferred for their uniformity. A polysaccharide cellulose chain is comprised of glucose units linked via β -1,4-glycosidic bonds, resulting in the alternating orientation of the individual monomers (figure 1.2). Each glucose A single strand of cellulose is estimated to contain between 100 - 200 glucose units, representing a molecular weight (MW) of 20,000-40,000 daltons [18].

Each monomeric repeat unit in the chain has three hydroxyl groups that form hydrogen bonds. When counting from the oxygen of the ring, fully nitrated NC posses a primary nitrate ester at carbon 6. Secondary nitrate esters are joined to the ring at carbon positions 2 and 3. Primary nitrates are those with one non-hydrogen moiety on the carbon, (additional to the nitrate linkage) with the remaining two bonds linked to hydrogens. Secondary nitrates are those where the nitrate carbon posses one bonded hydrogen atom, and two further non-hydrogen moieties. Carbons centres of tertiary nitrates posses no attached hydrogen, and are usually sterically hindered but as a result strongly stabilising to carbocations, favouring mononucleic mechanistic pathways.

In ordered regions of the cellulose matrix, the hydrogen bonds allow the chains to arrange in a sheet or fibril structure. In the disordered regions of the structure, these hydroxyl groups may be free or only weakly bonded, without a long-range hydrogen bonding

network. Water may also interact with these hydroxyl groups in the disordered region, introducing a susceptibility to hydrolysis in the chain. The oxygen in the glycosidic linkage between monomer units allows for rotation, introducing flexibility in the polymer chain via twisting and bending motions.

In addition to molecular and microstructural properties leading to variation in the decomposition of NC, it was shown by Wei *et al.* that the macroscopic bulk preparation of NC as soft fibres or as chips also changed the reactivity [19]. The soft fibre structure was found to be more easily ignited, possibly due to the less compact preparation leading to increased surface exposure to oxygen, higher porosity to reactants and easier penetration of the environmental effects, such as increased rate of heating due to lower density. This highlights the holistic perspective that must be taken when evaluating the spectrum of factors and properties responsible for the decomposition behaviour of any given sample of NC.

1.3 Nitrocellulose degradation

As in the case of its parent molecule cellulose, NC is largely insoluble in water, though recent studies have successfully synthesised a ‘high solubility’ variety using unconventional cellulose feedstocks [20]. Due to the insolubility of cellulose esters in general, the addition of plasticisers are necessary to encourage malleability for processing **Golubev2015!** (**Golubev2015!**). The properties of an NC formulation therefore depend on extent of nitration, the molar mass and crucially, the plasticiser level [21]. NC is extremely flammable when dry and so is usually kept in solvent to prevent detonation when under storage.^{18,19} Mixed with at least 25 % of water or alcohol, NC is completely stabilised [22]. This has facilitated the use of aqueous solvents as dispersion and transport mediums in manufacturing processes, leading to small NC fibres, or “fines”, in output streams. Demilitarisation activities have resulted in large volumes of NC waste which regulatory action now prevents the disposal of via incineration [23, 24, 25, 26]. A high level of side group substitution relative to cellulose, in addition to its insolubility, contributes to resistance to microbial degradation [27, 28]. As a result, NC exhibits poor mobility and a long lifetime in the environment. A detailed understanding of the degradation mechanisms is imperative in the design of efficient and economical processes for NC disposal. Whilst many studies in the past century have shed light on the various decomposition schemes, a review of the literature reveals conflicting conclusions on the general mechanisms of decomposition via alkaline hydrolysis, acidic hydrolysis, thermolysis and biodegradation treatments. Most notably, a distinct

lack of mechanistic detail hinders improvement of the processing and storage treatments, or effective redirection of degradation products to more useful substances, such as plant fertiliser [23, 29]. Understanding of the mechanism is also crucial for control of the potential harmful materials released into the atmosphere as part of the ageing process. N₂O is a potent greenhouse gas but is a known decomposition product. It can be produced via a number of potential routes, including oxidation of released nitrate species. Knowledge of the key formation pathways would allow influence of formulations and storage conditions to limit N₂O release.

The computational studies of Shukla determined that denitration occurred before the peeling off reaction of monomeric units, or rupture of the glucopyranose rings [30, 31]. Whilst IR spectra recorded by Pfeil and Eisenreich showed that slow heating of 1.4% H₂O, 13.3%N NC induced no self-heating, and rather, exhibited a decrease in the molecular weight before any decrease in the nitrate peak was observed [32]. This directly contradicts the conclusions of Shukla, as it would suggest that the peeling off reaction, or chain scission of the polymer, occurs before any denitration. They state that while the decay of the concentration of the nitrate is autocatalytic, as its decay up to 450 K is small, it can be treated as first order.

The alkaline hydrolysis reactions of NC have undergone thorough study due to their central role in large-scale NC disposal from manufacturing waste streams. It was realised early on by Kenyon and Gray that the action of alkalis on NC did not just yield cellulose and the corresponding metal nitrate salt, but a whole mixture of highly variable organic and inorganic products [33]. Miles observed that whilst acid and alkaline hydrolysis both produced similar products, the rate of the latter reaction was much greater [34]. Typically, NC is treated with concentrated sodium hydroxide and heating. Though other alkalis maybe used, such as. barium hydroxide, calcium hydroxide or sodium carbonate, these alternative alkalis require longer contact and heating times in addition to a larger measure of alkali to dissolve the NC [35]. In 1976 Wendt and Kaplan reported that a sodium hydroxide solution of 3 % by weight at 95 °C was able to effectively degrade NC of 12.6-13.4 %N to completion, in only 30 minutes. Su and Christodoulatos observe a similar rate, with 90 % of digestion occurring within 35 minutes, in 2 % sodium hydroxide at 70 °C for NC of 12.2 %N [36]. Multiple studies demonstrate that microbial biodegradation is an effective method of degrading NC [37]. Wendt and Kaplan's study presented a bench-scale continuous treatment

process involving initial degradation by alkaline hydrolysis followed by biological digestion using naturally occurring microbes in raw wastewater, for which they acquired a patent a year earlier [38]. It was noted by Fan *et al.* that highly substituted cellulose derivatives are resistant to direct biodegradation and require pre-treatment. Work on the enzymatic hydrolysis of cellulose revealed that increasing the crystallinity of the substrate reduced its digestibility [39]. This is reinforced in the study by Mittal *et al.* involving alkaline and liquid-ammonia treatments on crystalline cellulose [40]. Substitution of hydroxyl groups to increase solubility of cellulose derivatives lead to increased enzymatic hydrolysis, up to complete solubilisation. After this point, susceptibility slowly decreased. As solubility was no longer the limiting property, further increase in substitution began to inhibit digestion. It may be that as the levels of substitution increase, polymer geometries become less suited to the active sites of enzymes involved in degradation.

The IR and C¹³ nuclear magnetic resonance spectroscopy (NMR) studies coupled with roentgenographs of the NC structure at different levels of nitration showed that the cellulose backbone became more ordered with accumulating levels of nitrogen [41] Globular structures in bulk NC with 8 %N were converted to fibrils as the nitrogen content increased. A relatively high degree of ordering within the bulk is observed at 13%N, facilitating significant interaction between chains, contributing to increased hydrogen bonding between chains. Kim *et al.* explored the possibility of combining acid hydrolysis with biodegradation on an industrial scale. Feasibility of the hydrolysis reaction using hydrochloric acid with heat, was thoroughly investigated [22]. The study assumes that the nitrate group of C6 reacts the fastest, reasoning that groups on C2 and C3 experience more steric hindrance. The much later computational study by Shukla disagrees, finding that the C3 nitrate is the first to be liberated [30, 31].

Kim achieved denitration by treatment with acid more dilute than that initially used to synthesise the NC sample. A lower concentration of acid promoted shift of the equilibrium towards denitration. Though glucose was the major product of the monitored denitration process, it was stated that the rate of denitration was more rapid than the peeling-off reaction. In theory, it should be possible to regenerate strands of cellulose under the appropriate conditions. However, results only focussed on the retrieval of end-stage hydrolysis products such as glucose, nitrates, nitrites and ammonia. In addition, acid catalysed side reactions may introduce complications. However, Baker and Easty stated that alkaline hydrolysis was

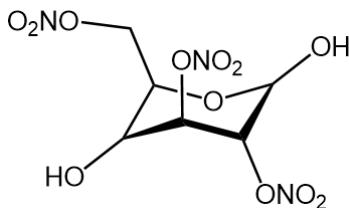


Figure 1.4: The work of Shukla *et al.* employed 2,3,6-trinitro-beta-glucopyranose as a monomer for NC [30, 31, 46].

on the order of 480 times faster than acid hydrolysis [42]. Though less studied than alkaline hydrolysis and deemed a slower process, the acid hydrolysis mechanism is extremely important for the understanding of decomposition and ageing processes of NC, as a residual amount of acid always remains in the system. Products liberated via other breakdown routes also go on to form acidic species within the environment and contribute to further decomposition via secondary reactions and autocatalysis [43]. Assary stated that acid catalysed decomposition of sugars in aqueous medium were initiated by protonation at hydroxyl groups [44]. This is later was later observed computationally by Feng *et al.*, where intramolecular hydrogen transfers, dehydration reactions, and ring-opening processes resulted from protonation of hydroxyl groups at specific sites on the sugars [45].

1.3.1 Computational Studies

A review of published works yields very few NC mechanistic degradation studies involving computational methods. Due to the nature of the topic, many of the referenced works above are linked with private or military organisations. Thus, their release may be restricted until declassified many years later, or completely withheld. The timeline of much of the material reviewed here ranges from mid to late 1900s, before the widespread use of computational methods in chemical research. Consequently, it is to be expected that more NC computational studies will appear in the near future. As discussed above, Shukla *et al.* performed a series of mechanistic studies on 2,3,6-trinitro- β -glucopyranose (figure ??), exploring its validity as monomer model for the NC polymer during alkaline hydrolysis via the saponification route [30, 31, 46]. If the hydrolysis reaction were to proceed via the saponification route, in practice it is unlikely that all nitro groups are liberated simultaneously. The work examined the possible sequences of nitrate group removal for a fully nitrated NC polymer in the hydrolysis reaction, in addition to whether denitration, depolymerisation or rupture of the ring would initiate. It was reported that nitrate groups would undergo an SN2! (SN2!) substitution reaction whereby each nitrate ester group is replaced by the incoming hydrox-

ide nucleophile, liberating a nitrate ion. Calculated enthalpies and free energies indicated a $\text{C}_3 \rightarrow \text{C}_2 \rightarrow \text{C}_6$ sequence of denitration for the monomeric unit. Their later work involving the dimer and trimer models suggests a significant change in behaviour when scaling up from the monomer. Dimer and trimer activation energies proved comparable, but showed an inconsistency with the monomer, instead exhibiting a $\text{C}_3 \rightarrow \text{C}_6 \rightarrow \text{C}_2$ sequence. There is the problem that the latter sequence was derived only from the energies of the initial nitrate removal step, whereas the monomer sequence was derived from energies calculated at each of the three stages of denitration. As there is little disparity between the dimer and trimer energies, but a large difference to the monomer results, it was said that the dimer should be the smallest unit used to describe the alkaline hydrolysis behaviour of NC. Though not a study involving NC, detailed work on the nitrate ester degradation routes in pentaerythritol tetranitrate (PETN) was conducted by Tsyshevsky, Sharia and Kuklja [47]. PETN is an energetic material possessing four nitroester moieties. Similarly to NG, it is used as both an explosive and in medicine [48]. Existing experimental activation energies for decomposition were scattered in the range of 30 to 70 kJ mol^{-1} . The group attributed the dispersion in data to inconsistent procedures and experimental conditions between studies. The most common degradation products recorded were CO , CO_2 , NO , N_2O , CH_2O , HCN , and HNCO . Echoing earlier NC and other nitroester thermolysis studies [49], the first degradation step was assumed to be nitrate ester homolytic fission. Activation barriers calculated using PBE, PBE0 and wB97XD were compared, finding that homolytic cleavage of the $\text{O}-\text{NO}_2$ bond was most favourable due to the fastest rate of reaction. The competing elimination of nitrous acid possessed an activation barrier of only approximately 6 kcal mol^{-1} but was slower. However, this second reaction was also exothermic, and through bulk calculations it was determined the secondary reaction would accelerate global processes *via* self-heating. Analyses of the implemented functionals found that PBE consistently underestimated barrier height by 12 to 14 kcal mol^{-1} on average, with respect to the remaining methods used, but all methods give good agreement for the energies of reaction.

1.4 Motivation

Despite its long history, NC is still an essential ingredient in many propellant and lacquer formulations. Efforts have been made to substitute it with other polymeric binders in attempt to reduce the manufacturing risk it poses due to its volatility, but this has only been partly successful [50]. NC, amongst other EM have caused many thermal runaway reactions,

leading to accidents and explosions worldwide. Insufficient understanding of the internal processes leading to the root causes of thermal instability has led to accidents in the past, sometimes resulting in property damage and in the most severe cases, lives lost [51, 52, 53, 19, 54, 55]. It is therefore imperative that we seek to clarify our understanding of the ageing mechanisms to inform the reduction of associated risks, whilst more effectively preserving existing NC stock.

Changing policy on the use of genetically modified (GM) crops may impact the NC supply chain. Cotton linters provide the highest grade cellulose for military and industrial grade production. As this feedstock diminishes in availability or quality, alternative sources, such as lower quality softwood pulp, may be substituted. Experimental studies over the past 100 years have shed light on the macroscopic degradation behaviour of bulk NC. However, the fine mechanistic details of degradation have only been alluded to, and are as yet unvalidated. Identifying a clear map of the possible reactions that occur during ageing will promote adaptability against a variable cellulose feedstock, and facilitate understanding of the possible changes in chemical properties for different batch lines.

In this study we will elucidate the dominant degradation schemes in NC with scrutiny of previously proposed decomposition pathways, and present new mechanistic considerations. This will be achieved via the application of computational techniques to give insight where it has been restricted by the limitations of laboratory experimentation in the past.

1.5 Research objectives

In this thesis the dominating degradation reactions that occur in NC are investigated. The objectives of this study is as follows:

1. Determine a representative system for modelling the degradation chemistry of NC.
2. Understand the denitration sequence in NC and compare to experimental observations.
3. Elucidate the initial degradation reactions that occurred in the slow ageing on NC.
4. Map the secondary reactions that occur in NC and explain the change from pseudo first-order to autocatalytic rate of degradation.

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