

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

G09	Gaussian 09 revision D.01
GM	genetically modified
GView	Gauss View 5.0.8
HF	Hartree Fock theory
HMF	hydroxymethylfurfural
HOMO	highest occupied molecular orbital
IR	infra-red spectroscopy
MD	molecular dynamics
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
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 A brief history of Nitrocellulose

NC, cellulose nitrate, or “guncotton” is a nitrated cellulose derivative (figure 1.1) that has been widely utilised in the manufacture of plastics, inks, propellant formulations and thin films since its discovery in 1833 by Henri Braconnot [1].

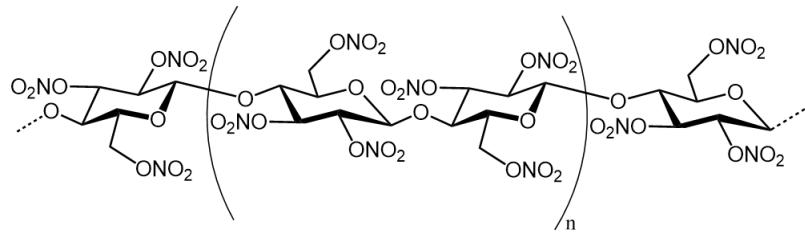


Figure 1.1: The structure of Nitrocellulose.

Cellulose is the primary component of plant cell walls and the most abundant polymer in nature [2, 3]. An example is cotton, which is almost entirely comprised of cellulose [4]. 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 [5, 6, 7, 8]. Bio-plastic products utilising thin films made of cellulose derivatives, such as NatureflexTM [9], have emerged in the consumer market offering attractive replacements to traditional crude-oil plastics (figure 1.2). These alternatives provide biodegradable food packing films, 3D printing elements, wound dressings and film-blown plastics, spanning almost the full range of current applications. Whilst the durability of cellulose-based products may not yet meet that of their plastic counterparts, they come with the key advantage of compostability. This facilitates their secondary use as an organic feedstock, such as in fertiliser for



Figure 1.2: Comparison of degradation times for Natureflex™ bioplastic against conventional plastic packaging, from The Mindful Chef blog [8].

agricultural applications, fostering a circular carbon economy [10].

It was found by Braconnot that when fibres of cellulose 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 [11]. He named this material xyloidine [12]. In his Berlin laboratory in 1845, Dr. Schönbein serendipitously discovered that acid treated cotton wool burned violently, and was the first to obtain a stable product using a mixture of nitric and sulfuric acids [13]. He was granted a U.S. patent the following year, and variations of his technique are currently still used in the commercial manufacture of nitrocellulose (NC) [14, 15].

Subsequent progress in the synthesis of stable NC products followed this discovery:

1855 - George Audemars pulls a NC filament from solution of ether and alcohol [14].

1864 - Baron Lenk patents a method for producing “improved guncotton” [16].

1866 - British chemist Frederick Abel patents another method for manufacturing NC, this time removing impurities and generating a more stable product, establishing its commercial importance [17].

1868 - John Wesley Hyatt combines NC with camphor to produce one of the first plastics, celluloid. This is later used to make billiard balls, which were previously made from ivory [14].

1883 - Whilst working on an early version of the lightbulb, Joseph Swan develops a method of extruding nitrocellulose into filaments [14].

1884 - Paul Vielle invents the first NC-based smokeless gunpowder [12].

1.1.1 Applications

NC is commonly found in adhesives, paints and lacquer coatings [18, 19]. Since Schönbein's day, NC has seen applications in dynamite, artificial silks and printing inks. Reels of historical cinematographic film made from NC were notoriously flammable, banned on public transport, and permitted storage and use only within fire-proof projection boxes [20, 21, 22, 23]. Conservation efforts attempted to preserve these materials *via* cold storage or duplication onto more stable cellulose triacetate or polyester films. For heavily deteriorated film, destruction was recommended due to fire and safety hazards [24, 20]. Today, the information on NC films is preserved by digitisation [25].

Collodin, a solution of NC in either ether or ethanol, is used both in surgical dressings and in theatrical make-up. To create special effects, a non-flexible variety of colloidin is applied to skin, which puckers as the solvent evaporates, effectively creating the appearance of scarred tissue. NC thin films also perform an essential role in research. Tonkinson and Stillman produced a review on the merits of NC film in blotting practices, utilised as a microporous membranes in genomic experiments for decades [26]. Finding that it could bind DNA-RNA duplexes in solution, the first application of NC in molecular biology was as a molecular sieve to separate DNA duplexes from free RNA. Later work exploited this property to study protein-DNA interactions.

Varieties of high percentage nitrogen by mass (%N) are used for their energetic properties, such as in rocket and gun propellants. NC of above 12.5 %N is considered explosive (figure 1.3). The theoretical maximum level of nitration is 14.14 %N. This corresponds to a degree of substitution (DOS) of three, where each of the three free hydroxyl groups has been replaced by a nitrate ester (equation 1.1, figure 1.3). In practice, only a maximum of 13.6 - 13.8 %N (DOS=2.9) is routinely achieved [27, 28], though higher, unstable levels of nitration have been obtained at high temperatures [12].

$$\text{Degree of substitution (DOS)} = \frac{3.6 \times \text{nitrogen content (\%)}}{31.13 - \text{nitrogen content (\%)}} \quad (1.1)$$

DOS values do not directly correlate to the exact level of nitration at each monomeric site due to the imprecision during the nitration reaction; the approximate %N corresponding to each level of nitration is given in table 1.1. A non-integer value for DOS indicates non-uniform nitration on individual glucopyranose rings throughout the polymer structure.

When NC is the only energetic component in an explosive mixture, it is termed a

Table 1.1: DOS in NC and the corresponding percentage nitrogen by mass (%N).

DOS	%N	Description
1	6.76	Cellulose mononitrate
2	11.11	Cellulose dinitrate
3	14.14	Cellulose trinitrate

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.

The behaviour and ageing of NC within product formulations depends on the structure and degree of nitration of the material itself, in addition to the environmental and storage conditions, and interactions with any plasticisers and stabilisers in the product mixture.

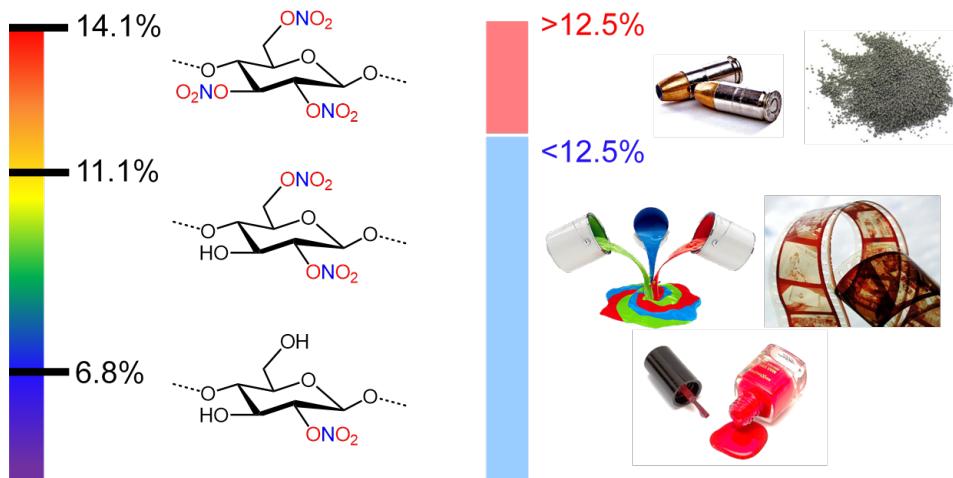


Figure 1.3: Left: The percentage nitrogen by mass (%N) of NC corresponding to each degree of substitution (DOS).

Right: NC with lower levels of nitration play a role in the manufacture of paints and lacquer coatings, whilst $<12.5\%\text{N}$ is used in the production of explosives and propellants.

1.2 Synthesis and structure

Nitrocellulose is derived from the nitration of cellulose. Biological variation in cellulose has implications on the quality and properties of the NC produced. During synthesis, the backbone of cellulose is largely preserved [29, 30]. 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. Cotton sources are usually reserved for the production

of military and industrial grade propellants, with pulps from softwoods used for manufacture of explosives used in blasting and mining operations [31]. A polysaccharide cellulose chain is comprised of glucose units linked via β -1,4-glycosidic bonds, resulting in the alternating orientation of individual monomers. This is then reflected in the synthesised NC structure (figure 1.4). 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 [14]. Each monomeric repeat unit in the chain has three hydroxyl groups that form hydrogen bonds. In ordered regions of the cellulose matrix, the hydrogen bonds allow the chains to arrange in a sheet or fibril structure.

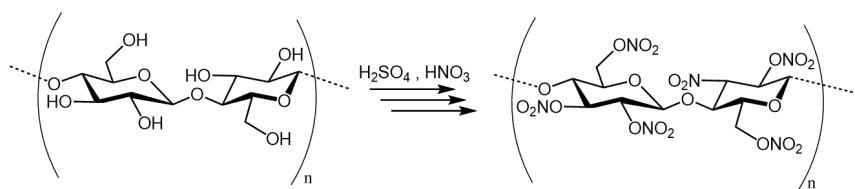


Figure 1.4: Cellulose is converted to NC by a mixture of nitric and sulfuric acids.

For the conversion of cellulose to NC, a common nitrating mixture of nitric and sulfuric acids is used to generate the nitronium ion (equation 1.2). The nitronium ion is attacked by the lone pair on the oxygen of the hydroxyl group on cellulose, leading to the formation of a nitrate ester (equation 1.3 and figure 1.5).



Where R = Cellulosic backbone

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-

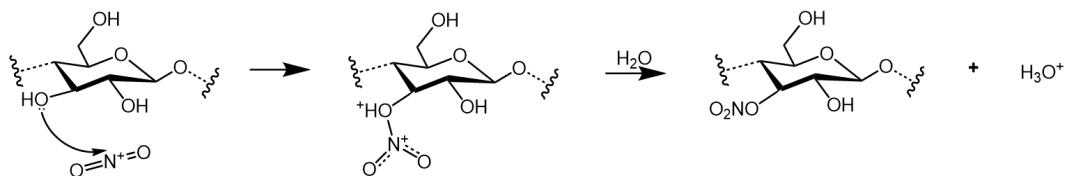


Figure 1.5: Nitration of cellulose by the nitronium ion.

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. 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.

The IR and C¹³ nuclear magnetic resonance spectroscopy (NMR) studies coupled with x-ray images of the NC structure at different levels of nitration showed that the cellulose backbone became more ordered with accumulating levels of nitrogen [32]. 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. In the disordered regions of the structure the hydroxyl groups may be free or only weakly bonded, without a long-range hydrogen bonding network. Water may also more easily interact with these hydroxyl groups in the disordered region, introducing an increased susceptibility to hydrolysis within 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.

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 [33]. Due to the insolubility of cellulose esters in general, the addition of plasticisers are necessary to encourage malleability for processing [34]. The properties of a NC formulation therefore depend on extent of nitration, the molar mass, and crucially, the plasticiser level [35].

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 [36]. 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 emphasises 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

Even under optimal storage conditions, NC undergoes slow decomposition over time. A detailed understanding of these 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 opinion on the general mechanisms of degradation. Most notably, a distinct lack of mechanistic detail hinders improvement of processing and storage treatments, or effective redirection of degradation products to more useful substances, such as plant fertiliser [37, 38].

Understanding of the mechanism is also crucial for control of the harmful materials released into the atmosphere as part of disposal or the ageing process. Traditional methods of disposal usually include incineration of waste NC (figure 1.6) [39]. In order to limit safety risks, propellants are often burned as an aqueous suspension. Specialised equipment (figure 1.7) allows sequential evaporation of water, drying, followed by ignition of the propellant within a controlled manner. Combustion gases are then scrubbed with water before release into the environment [40].

Due to regulation on incineration as a waste disposal method, experimentation with treatments such as alkaline hydrolysis, acidic hydrolysis, photochemical, biodegradation, mechanical or combined methods have also been studied as an alternative techniques for removal.

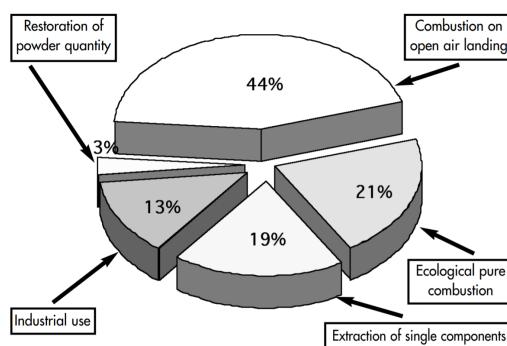


Figure 1.6: The fate of waste NC powders discarded from military stocks. The majority undergoes a form of combustion. From the work of Ganev *et al.* [41].

1.3.1 Hydrolysis degradation methods

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 cor-

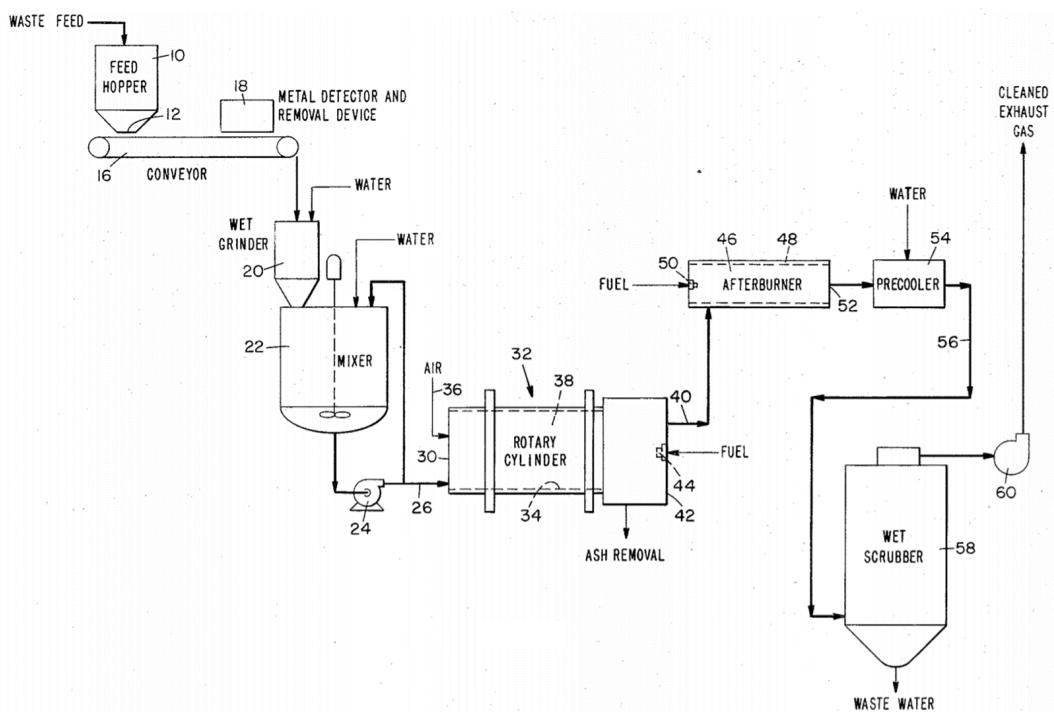


Figure 1.7: Schematic of an incinerator designed for the destruction of waste explosives, patented by Bolejack *et al.* [40].

responding metal nitrate salt, but a whole mixture of highly variable organic and inorganic products [42]. Miles observed that whilst acid and alkaline hydrolysis both produced similar products, the rate of the latter reaction was much greater [43]. Baker and Easty stated that alkaline hydrolysis was on the order of 480 times faster than acid hydrolysis [44]. Typically, NC is treated with concentrated sodium hydroxide and heated. 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 [45]. 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 [46].

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. “Spent” or residual acids always remain in the system from incomplete washing following synthesis. Products liberated *via* other breakdown routes also

go on to form acidic species within the local environment, and contribute to more extensive decomposition via secondary reactions and autocatalysis [47]. Assary stated that acid catalysed decomposition of sugars in aqueous medium were initiated by protonation at hydroxyl groups [48]. This 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 various sugars [49].

The study of Kim *et al.* explored the possibility of combining acid hydrolysis with biodegradation on an industrial scale [50]. Feasibility of the hydrolysis reaction using hydrochloric acid with heat, was thoroughly investigated. Kim achieved denitration by treatment with acid more dilute than that initially used to synthesise the NC sample. The study assumed that the nitrate group of C6 reacted the fastest, reasoning that groups on C2 and C3 experience more steric hindrance. A lower concentration of acid promoted shift of the equilibrium towards denitration. In addition, acid catalysed side reactions may introduce complications. 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, these results only focussed on the retrieval of end-stage hydrolysis products such as glucose, nitrates, nitrites and ammonia.

1.3.2 Biological degradation methods

Multiple studies demonstrate that microbial biodegradation is an effective method of degrading NC [51]. 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 [52]. It was noted by Fan *et al.* that highly substituted cellulose derivatives were 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 [53]. This is reinforced in the study by Mittal *et al.* involving alkaline and liquid-ammonia treatments on crystalline cellulose [54]. Substitution of hydroxyl groups to increase solubility of cellulose derivatives lead to increased enzymatic hydrolysis, up to complete solubilisation. After this point, susceptibility to biodegradation slowly decreased. As solubility was no longer the limiting property, further increase in substitution began to inhibit enzymatic digestion. It may be that as the levels of substitution increase, polymer

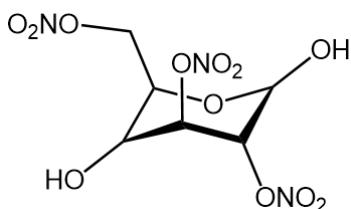


Figure 1.8: The work of Shukla *et al.* employed 2,3,6-trinitro-β-glucopyranose as a monomer for NC [55, 56, 57].

geometries become less suited to the active sites of enzymes involved in degradation.

1.3.3 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 conjunction with experimental chemical research. Consequently, it is to be expected that more NC computational studies will appear in the near future. Shukla *et al.* performed a series of mechanistic studies on 2,3,6-trinitro- β -glucopyranose (figure 1.8), exploring its validity as monomer model for the NC polymer during alkaline hydrolysis via the saponification route, whereby the nitrate ester was cleaved to restore the hydroxyl group and the nitrate salt [55, 56, 57]. 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 bi-molecular nucleophilic substitution reaction (S_N2) substitution reaction whereby each nitrate ester group is replaced by the incoming hydroxide nucleophile, liberating a nitrate ion. Calculated enthalpies and free energies indicated a C3 → C2 → C6 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 C3 → C6 → C2 sequence. There is the problem that the latter sequence for the dimer and trimer was extrapolated only from the energies required to remove the first nitrate group. In contrast, the monomeric sequence was derived from energies calcu-

lated at each of the three stages of nitrate removal; the reaction energy was evaluated for sequential cleavage starting with a different nitrate site each time. 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 was the smallest unit able to adequately 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 [58]. PETN is an energetic material possessing four nitroester moieties. Similarly to NG, it is used as both an explosive and in medicine [59]. Existing experimental activation energies for decomposition were scattered in the range of 30 to 70 kCal 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, CO₂, NO, N₂O, CH₂O, HCN, and HNCO. Echoing earlier NC and other nitroester thermolysis studies [60], 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 O–NO₂ bond was most favourable due to the fastest rate of reaction. The competing elimination of nitrous acid possessed a lower 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 that all methods give good agreement for the energies of reaction.

1.4 Environmental impact of NC waste products

NC is extremely flammable when dry and so is usually kept in solvent to prevent detonation when under storage [61, 62]. Mixed with at least 25 % of water or alcohol, NC is completely stabilised [50]. 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 [37, 63, 64, 65]. A high level of side group substitution relative to cellulose, in addition to its insolubility, contributes to resistance to microbial degradation [66, 67]. As a result, NC exhibits poor mobility and a long lifetime in the environment.

Burning releases a myriad of toxic and harmful products into the atmosphere [41]. N₂O is a potent greenhouse gas but is a known decomposition product. It can be produced via a number of potential mechanistic routes, including oxidation of liberated nitrate species. Knowledge of the key formation pathways would allow manipulation of product formulations and storage conditions to limit N₂O release.

Whilst NC itself is relatively harmless to most mammals, macroinvertebrates, fish and algae [68], this cannot be said for the effluents from NC production and any nitro byproducts. Nitration, bleaching and delignification solvents require treatment before discharge into the environment, due to toxicity to the aquatic environment [69, 70, 71]. In addition, the fibrous nature of small NC fines in wastewater can alter the natural habitat at the bottom of ponds and bodies of water, by covering and thus limiting the oxygen access to benthic organisms [68]. Although NC itself is unstable and degrades gradually over time, its insolubility means that decomposition under natural environmental conditions is slow, as in the case of discarded munitions or explosive residues [72].

1.5 Motivation

Despite its long history, NC is still an essential ingredient in many propellant and lacquer formulations today, with its versatility spanning an extensive range of products and applications. The diversity of its use means that we come into contact with it in some shape or form everyday. Whilst efforts have been made to substitute it with other polymeric binders in attempt to reduce the manufacturing risk it poses due to its volatility, this has only been partly successful [73].

NC, amongst other EM have caused many thermal runaway reactions, leading to accidents and explosions worldwide. Insufficient understanding of the internal processes has lead to unintended explosions during storage and at nitration industrial plants, and in the most severe cases, casualties [3, 74, 75, 36, 76, 77]. It is therefore imperative that we seek to clarify the understanding of the ageing mechanisms to inform the reduction of associated risks, whilst more effectively preserving existing NC stock.

NC disintegration is also of relevance in the preservation of historical artefacts and cinematographic film, where knowledge of the decomposition processes are crucial to the maintenance of items of historical value [20, 78].

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 indus-

trial 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 better understanding of the possible changes in chemical properties for different batch lines [31].

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.

1.6 Research objectives

In this thesis the dominant 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. Apply the model in the investigation of primary degradation reactions that occur in the slow ageing of NC.
3. Map the secondary reactions that occur in NC and shed light on the processes responsible for the autocatalytic rate of degradation.

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