Computational Study of the Ageing Processes in Nitrocellulose

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Declaration

I, Amy Lai , confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the work.

Abstract

My research is about stuff. It begins with a study of some stuff, and then some other stuff and things. There is a 300-word limit on your abstract.

Impact Statement

Some of the following will belong in the motivation section, rather than the IMPACT section.

- nitrocellulose (NC) has been used in many products and its important to know how they are ageing, especially for those with a propellant application.

- create new products, not limited by previous assumptions about the shelf life / reactivity etc (obviously this is a big generalisation. IT might be that the current industrial standards are ok / not too far off. But at least this might mean better/ more tailored / cheaper stabiliser / plasticiser formulations can be used, or things that are more readily available and more options, in case certain things become unavailable.)

- This means that next generation products could be more environmentally friendly / industrial process is more environmentally friendly, easier to dispose of, or more recyclable. It could mean that NC, which is not derived from petrochemicals / plastics, can help fight the plastic / waste disposal problem. It's non-toxic to humans (CHECK) and so in its degradation, could also help fight the micro-plastics ingestion problem, in the long term. (basically, polysaccharides, like PLA etc, could assist in the long term transition from petrochemical plastics to biodegradability. Though NC isn't necessary biodegradable without specific microbes found in the lab yet - better understanding of its breakdown could facility an easier process for this.)

- current industrial guidelines on safety and usage could be refined with better understanding of the actual reactions that take place, instead of a broad-brush style guidelines based on historical less precise experimental observations

- More agility in the production of NC, when the source cellulose feedstock change.

- More appropriate NC disposal methods, with opportunity to streamline to more environmentally friendly methods, or insert into/ modify industrial process to re-formulate into

other products, such as fertilisers etc. with leftover NC etc

 - table of the property/sector vs benefit. (See Tab. 1) This may or may not be relevant. ASK MAX about this one closer to the time.

Table 1: The impact of improving understanding of NC ageing processes

NC Application	Benefit
Medicine: Spray on bandages in health	Better predict lifetime of the product, and shed light on what stabilisers to use to extend usability time
Commercial & Defence: Ejection propellant in aircraft	Improve formulations, increase lifetime and heat resistivity of propellant mixture, decrease costs.
3	23.113231

In this study I do not present a complete solution to the myriad interlinked degradation reactions that are accountable for the decomposition behaviour of NC. Rather, this work elucidates the initial steps on the path towards full understanding of the ageing processes of NC

There is a 500-word limit on your impact statement.

Acknowledgements

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Abbreviations

B3LYP	Becke, 3-parameter, Lee-Yang-Parr hybrid functional
CP	critical point
DFT	density functional theory
DOS	degree of substitution
ESP	electrostatic potential
G09	Gaussian 09 D.01
GView	Gauss View 5.0.8
HF	Hartree Fock theory
MM	molecular mechanics
MW	molecular weight
NC	nitrocellulose
NG	nitroglycerine
NMR	nuclear magnetic resonance spectroscopy
QM	quantum mechanics
QTAIM	quantum theory of atoms in molecules
S$_N$2	bi-molecular nucleophilic substitution reaction

Chapter 1

Introduction

1.1   The modern history of 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. [PICTURE!]

Cellulose is the primary component of plant cell walls (REF). It was found (by who?) the when cellulose fibres, in the form of sawdust, cotton (linen) and paper were treated with nitric acid, (it was discovered that) the product burned rapidly and in the absence of the thick black smoke that was characteristic of gunpowder of the era.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. He was granted a U.S. patent the following year.

Today NC is present in adhesives, paints and lacquer coatings. Varieties of high percentage nitrogen by weight (%NMax) 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, printing inks and reels of old film, which were famously flammable. 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. [PICTURE!]

Cellulose is abundant in nature, however its biological variation has implications on the quality and properties of the NCit produces. During synthesis the backbone of cellulose is largely preserved (Figure conversion of C to NC).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.

NC of above 12.5 %NMax is considered explosive. The theoretical maximum level of nitration is 14.14 %NMax, corresponding to a degree of substitution (DOS) of three, where every free hydroxyl group has been replaced by a nitrate ester. In practice only 13.6 %NMax has be achieved. 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 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.

Some stuff about things.[?] Some more things.
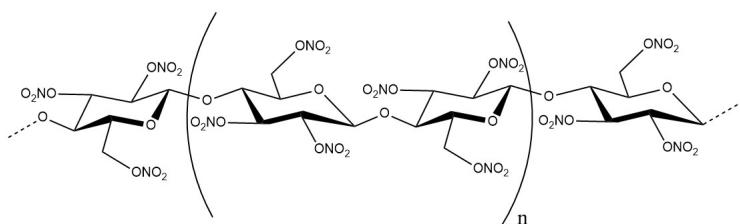
Figure 1.1: The structure of Nitrocellulose.

1.2   Applications

*Talk about the renewed interest in NC - see:

https://medium.com/@pandevedashri/global-nitrocellulose-market-is-estimated-to-grow-at-a-cagr-of-6-5-during-the-period-2019-2025-800e2942f316

and

https://medium.com/photography-and-film/thoughts-on-celluloid-c1a6744312bb

Draw a nice info graphic of stats all the uses of NC, and a paper interest graph demonstrating the increased mention of Nitrocellulose in publications, since the war.

(thought the latter is more a niche thing)* NC has been used widely in manufacturing, as a feedstock for lacquers, coatings, propellants and ....., It continues to be used in industry today, due to it's low cost and versatility. However, new

1.2.1   (Explosive, non-explosive

Cf. plane seat ejector propellant formulation - important to know whether it can withstand humidity and temperature cycling.

1.3   Synthesis and structure

Nitrocellulose is dervied from cellulose. Cellulose is a naturally occurring polysaccharide found primarily in plant cell walls. It is the main component of cotton (FIGX). The polysaccharide chain is comprised of glucose units linked via β-1,4-glycosidic bonds, resulting in the alternating orientation of the individual monomers (FIGX). 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.

cf James Tucker - A whole life assessment of extruded double base rocket propellants. - NC chapter on synthesis

1.4   Reactions of Nitrate Esters

Reactions of all nitrate esters in general, not just NC.

1.4.1   Thermolytic reactions

Incorporate all computational, experimental studies, with mechanistic detail where possible and reference to other industrially methods at the end.

1.4.2   Hydrolysis reactions

1.5   Nitrocellulose degradation

Now, which of the above are relevant to NC, and what additional ones happen in NC / are unique to NC?

Think - secondary reactions, synergy between different nitrate groups and other properties linked to the degradation of sugar / organic polymers.

Review of Degradation studies Intro to experimental studies - When, why, what, where, who and how. In subsequent sections, make sure to go into the "so what?"

NC is extremely flammable when dry but is largely insoluble in water, and 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.Accidents [He He Liu 2017 has a reference to an accident at TianJin, but you can find the news article] 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. A high level of side group substitution relative to cellulose, in addition

to its insolubility, contributes to resistance to microbial degradation. 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 (section 2.1) [CLEAN THIS UP] 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 optimisation of the practised treatments, or effective redirection of degradation products to more useful substances, such as plant fertiliser.

1.5.1 Industrial disposal methods

This can be a tack on, at the end to highlight the relevance of the NC system, applications and current modes of usage.

Include the industrial decomposition methodologies here (biological etc.) Include an overview of all, but keep the alkaline and acid

Discuss Alkaline hydrolysis in the context of industrial process. However we don't want this as a big thing, as we want this lit review tailored to the study, with the equivalent emphasis. More detail on the studies that look at this. Include computational studies where relevant(maybe making reference to the computational section) .

[HAVE TO CLEAN UP] 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.[28] Miles observed that whilst acid and alkaline hydrolysis both produced similar products, the rate of the latter reaction was much greater.[29] 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 solubilise the NC.[8] In 1976 Wendt and Kaplan reported that a sodium hydroxide solution of 3 % by weight at 95 oC was able to effectively degrade NC of 12.6-13.4 %NMax 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 oC for NC of 12.2 % NMax.[30] Multiple studies demonstrate that microbial biodegradation is an effec-

tive method of degrading NC.31 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 earlier25 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.32 This is reinforced in the study by Mittal et al. involving alkaline and liquid-ammonia treatments on crystalline cellulose.33 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. 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.20 The study assumes that the nitrate group of C6 reacts the fastest, reasoning that groups on C2 and C3 experience more steric hindrance. A much later computational study by Shukla disagrees, finding that the C3 nitrate is the first to be liberated.3 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. Though less studied than alkaline hydrolysis, 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.34

1.5.2 (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. Shukla et al. performed a series of mechanistic studies on 2,3,6-trinitro-β-glucopyranose (FIG. 3), exploring its validity as monomer model for the NC polymer during alkaline hydrolysis via the saponification route.[3,4,35] 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 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 (FIG. 4.) 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 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 (Figure 4).[10] PETN is an energetic material possessing four nitroester moieties. Similarly to NG, it is used as both an explosive and in medicine.

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, CO2, NO, N2O, CH2O, HCN, and HNCO. Echoing earlier NC and other nitroester thermolysis studies,36 the first degradation step was assumed to be nitrate ester homolytic fission. The seven mechanisms explored, corresponding to the labels in Figure 4, are detailed in equations (1) to (7): (1) (2) (3) (4) (5) (6) (7) (1) homolytic cleavage of the O-NO2 bond, (2) the elimination of nitrous acid (HONO) which is usually considered as a competing reaction to homolytic fission, (3) the nitro-nitrite rearrangement (OONO), (4) γ-attack, the encounter of a peripheral oxygen atom and the central C atom (5) the homolytic C-O bond cleavage and (6), (7) two variations of the homolytic C-C bond cleavage. Activation barriers calculated using PBE, PBE0 and wB97XD were compared, finding that reaction (1) proceeded without a barrier and was therefore most favourable. Reaction (2) possessed an activation barrier of only approximately 6 kcal mol-1. 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 functionals used found that PBE consistently underestimated barrier height by 12 to 14 kcal mol-1 on average, with respect to the remaining methods used. Transition states were optimised within GAUSSIAN, followed by an intrinsic reaction co-ordinate computation for each mechanism.

Ring fission vs denitration / post denitration reactions.

1.5.3 Acid hydrolysis

"Acid catalysed decomposition of sugar molecules in aqueous medium is initiated by the protonation of the hydroxyl groups." - Assary, Kim 2012 All the detail in literature that you can find on this. Summary of all acid hydrolysis reactions, including kinetics. Include computational studies where relevant. Elaborate on how acid is always present in the system and may be the main contributor to accelerated ageing. Why is this important to know about?

1.5.3.1 Autocatalysis

[REF] suggests it is NO2+ that is the catalytic species, which is reinforce by Knight and Barry [REF] who found that the elevated catalytic degradation rate was not observed for cellulose acetate. (Though it is postulated to undergo similar hydrolysis steps? [REF])

1.5.4 Post-denitration reactions

What do the hydrolysis products go off to do. Include computational studies where relevant.

1.6   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. Insufficient understanding of the internal processes within nitrocellulose has lead to accidents in the past, sometimes resulting in lives lost. 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.

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.

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.

Chapter 2

Theory and Implementation

Intro - Recap denitration sequence as per literature

2.1 Introduction

2.2 Electronic structure methods

Intro to the history spiel. What it is, where did it come from.

2.2.1 The Schrödinger Equation

2.2.2 Born-Oppenheimer Approximation

2.2.3 Hartree Fock

Hartree Fock Hartree Fock theory (HF)

2.2.3.1 Variational Principle

2.2.3.2 Open shell systems

[PLEASE REVAMP ALL OF THIS AND FILL IN DETAIL] The forced pairing of electrons of opposing spin into a shared orbital is referred to as the Restricted (RB3LYP) scheme. For systems without unpaired electrons, or "closed shell", this treatment is sufficient. For radicals and other species with unpaired electron spin such as transition metal complexes, an alternative model allowing singly occupied orbitals must be adopted. The Restricted-Open (ROB3LYP) scheme maintains electron pairing within orbitals except in the case of the highest occupied molecular orbital (HOMO). This is singly occupied. An alternative model is Unrestricted (UB3LYP), where all electrons are unpaired and reside in their own orbitals (Figure 9). A caveat of the unrestricted model is its susceptibility to spin contamination, which has consequences at large bond separations where the bond has not completely broken.

2.2.4   Electron correlation

2.2.5   Density functional theory

See here for a nice sum of the weaknesses: Some Fundamental Issues in Ground-State Density, Perdew 2009 (https://pubs.acs.org/doi/10.1021/ct800531s) Functional Theory: A Guide for the Perplexed [PLEASE REVAMP ALL OF THIS AND FILL IN DETAIL] Density functional theory derives from the Thomas-Femi-Dirac model, whereby the electron correlation is modelled via functionals of the electron density.38,39 The total energy is defined by functionals split into the following terms:

$$E = E^T + E^V + E^J + E^X C$$

Where E^T is the kinetic energy term, arising from electron motion; E^V is the potential energy term arising from nuclear-electron attraction and nuclear-nuclear repulsion; E^J is the columbic repulsion term arising from electron-electron repulsion and E^{XC} is the exchange correlation term containing the remainder of the electron-electron interactions. The first three terms are purely classical, and correspond to the classical energy of the charge distribution (ρ). The exchange term is non-classical encompasses the exchange energy due to the antisymmetry of the wavefunction, and dynamic correlation of electron motion. It can be further divided into the exchange and correlation components:

$$E^X C(r) = E^X(r) + E^C(r)$$

In the context of this report, the B3LYP functional will be used where the exchange is described as follows:

Here c_0 = 0.2, c_X = 0.72 and c_C = 0.81. The coefficient c_0 allows mixing of E_{HF^x} (Hartree Fock) and E_{LDA^x} (Local Density Approximation). E_{VWN3^C} (VWN3 local correlation) is mixed with E_{LYP^C} (Lee, Yang, Parr correlation function) via c_C. E_{B88^x} is Becke's gradient-corrected exchange functional.

ωB97x-d is a range separated hybrid with D (self consistent exchange). It is more computationally demanding than just post HF style perturbation theory exchange (as in B3LYP, using MP2 exchange for example - fact check that). And according to the paper by Najibi and Goerigk even the D3 correction isn't better than the perturbation theory style exchange, for a massive amount of datasets that they tested. SO why even use this in the

first place? Look to the origianl paper where it was published and see how they tout this method. Use those reasons to justify having chosen it to use on some of my systems.

2.2.5.1 Hohenburg-Kohn formalism

2.2.5.2 Kohn-Sham Equations

2.2.5.3 Exchange-correlation functionals

2.2.5.4 Dispersion correction

Grimme

2.2.6 Basis sets

[FIX ME] A basis set is the collection of mathematical basis functions used in linear combination to construct the molecular orbitals. Split valence basis sets describe the core electrons with fewer basis functions than the interacting valence electrons, as they are not as significant in bonding or intermolecular interactions. In this study, the widely used Pople basis sets will be applied (Table 1. Examples of split valence basis sets.).[40,41]

Basis set superposition error (BSSE) is a false lowering of the energy that can occur when two species in a system approach one another to form a complex. Particle A borrows the extra basis functions belonging to particle B and an artificial stabilisation is observed. The error arises from the inconsistency in treatment between the individual particles at long separations and the complex at short distances. The effect is particularly pronounced for smaller basis sets. Counterpoise correction I used to circumvent BSSE, at the expense of higher computational resources required for the calculation.

2.2.7 (Transition State Theory & Free Energy Calculations)

2.2.8 Solvent models

2.3 Analysis

2.3.1 (Transition state searches)

[Maybe this goes into a smaller metholodgy section?] Transition state searches are called through the Opt=TS, QST or QST3 keywords. The Opt=TS method in GAUSSIAN attempts to optimise the given "guess" geometry to a transition state. The guess structure can be obtained from a geometry scan, manually constructed or generated using the QST2 function. In many cases, a TS alone will not be able to isolate the suitable transition state and is usually used in conjunction the QST2 or QST3 methods, and combined with other techniques such as frequency calculations. The QST2 option is able to generate a transition

state geometry using the Synchronous Transit Quasi-Newton (STQN) method42. Here the transition geometry is midway between a given reactant and product. The corresponding atoms labels must match in both the starting and end products. QST3 performs similarly, but also considers a guess transition state (Figure 10). It is widely acknowledged that transition state searching is challenging; in addition to the techniques above, the task requires perhaps a certain measure of chemical intuition.

Frequency calculations

2.3.2 (Intrinsic Reaction Coordinate)

[Maybe this goes into a smaller metholodgy section?] IRC calculations begin at the saddle point and descend the PES in both the forwards and backwards direction of the reaction co-ordinate dictated by the normal mode of the imaginary frequency. In a similar manner to a geometry scan, geometry optimisations are performed at each step point. Its purpose is to connect the two minima leading to the found transition state, thereby confirming whether the found transition state corresponds to your reactants and products of interest. IRC calculations are called via the IRC keyword, with specifications of whether the forward or backward reaction is to be scanned, step size and maximum number of steps allowed.

2.3.3 (PES Scans)

[Maybe this goes into a smaller methodology section?] Relaxed potential energy surface (PES) scans, or geometry scans are used to probe the local energy landscape corresponding to specific change in geometry. During the course of a scan, a selected bond length, angle or dihedral is adjusted in incremental steps, as specified by the given scan parameters. At each step, the adjusted parameter is frozen and a geometry optimisation is performed, allowing the rest of the system to relax around the modified bond. Each scan yields a PES of the explored pathway, presented in a reaction co-ordinate diagram (see Figure 17, section 2.4.1). An energy maximum followed by a trough indicates a transition state and intermediate reaction product, respectively. The structural co-ordinates at the points of interest are extracted and used for subsequent frequency calculations, transition state searches and validated using intrinsic reaction co-ordinate methods. To explore the predicted degradation mechanisms, the scanning parameter was assigned to the bond undergoing the most significant transformation during a particular step of the mechanism. In the case that more than one significant bond was altered, multiple scans with different bond specifications were compared. Geometry scans were performed on the optimised reactant geometry using the

Opt=ModRedundant keyword.

2.3.4   Nuclear Magnetic Resonance Spectra

Refer them to an actual resource, so you don't have to explain the theory of nuclear magnetic resonance spectroscopy (NMR), but give an overview of the experimental, then give the theoretical detail about how Gaussian calculates it, and any discrepancies between experimental and calculated.

Comment on the different methods used to calculate NMR parameters - a tiny literature review, if you will, and say which you'll be using, why - even if it's becuase of the fact that it's built into Gaussian (obviously big it up, if that is the case) - and state any caveats.

Maybe have a look at: Accurate Calculation of NMR Chemical Shifts, Jurgen Gauss, 1995 as a basis, but you'll also need something more current. Any review papers out there?

2.3.5   Infra-Red Spectra

Intro to the history spiel.

Chapter 3

Building the Model

3.1 Introduction

A wide range reaction products are experimentally observed during the low temperature degradation and slow ageing of NC. These can be partially attributed to the range of susceptible attack/ cleavage/ reactive sites points on the polysaccharide backbone, as well as the myriad of possible secondary reactions following denitration, depolymerisation or ring-cleavage. (When probing the details of individual chemical reactions using computational methods, the extended polymer structure becomes unweildy due to the large number of atoms.

In practice, *ab initio* and density functional methods used to determine the reaction energies are limited to between XX - XX atoms. The NC chain was truncated to a single-ring monomer by Shukla *et al.* for the purposes of investigating alkaline hydrolysis. [1] The study analysed the S_N2 nucleophilic attack at the nitrate carbon, releasing the nitrate ion in favour of a hydroxyl group, at the C2, C3 and C6 nitrate sites (FIG. X).

Insert fig X

Comparisons between the monomer, dimer and trimer found the dimeric structure to be the minimum model required to accurately represent the chemical behaviour of NC in the alkaline hydrolysis pathway.

3.2 Methodology

Monomer, dimer and trimer starting structures were drawn as closely matching literature geometries as possible. For dimer and above, individual saccharide rings were alternating (FIG) as in cellulose chains "observed during SEM / X-ray diff measurements" (FIG).

In order to explore the limitations of different capping groups, chain ends were capped

with either methoxy or hydroxy groups (FIG.), as were employed in Shukla's study. The differences in the charge distribution and intra-molecular interactions were probed using quantum theory of atoms in molecules (QTAIM) methods to look at critical points and the Laplacian of electron density. When regarding partial charges and to a limited extent, steric considerations, methoxy groups were expected to provide a better approximation for the extended polysaccharide.

Strucutres underwent geometry optimisation in vacuum and implicit solvent, using various methods detailed in section XX .

3.2.1 Computational details

All geometry optimisation was performed to the level of B3LYP 6-311+G(d,p), using Gaussian 09 D.01 (G09).

Structures were built either using z-matrix notation or using the **Gview!** (**Gview!**) graphical interface. electrostatic potential (ESP) surface maps were also visualised using G09, using the CubeGen utility.

The QTAIM analyses, including generation of Laplacian electron density maps and critical point (CP) analysis on the optimised structures were performed using MultiWFN 3.6

Molden 5.0.2 and Gauss View 5.0.8 (GView) packages were used for visualisation

3.3 Results & Discussion

3.3.1 Choice of functional

Discuss the validity and caveats of each methods, including solvent vs vacuum.

3.3.2 Electr

- Show the

[FIX ME]

All electronic structure and reaction pathway calculations were implemented in GAUS-SIAN 09 revision d01. Partial charges were obtained via PyRed (R.E.D. Server version 3.0). To circumvent the effects of BSSE, the largest computationally feasible basis sets are chosen and diffuse functions are included. A number of preliminary calculations were performed both with and without counterpoise correction (CP) to evaluate any inconsisten-cies. All studies were performed in the gaseous phase and initial structures were geometry optimised with B3LYP/6-311+G(d,p) and tight convergence criteria. Any incomplete or

unconverged optimisations were restarted with generation of new internal co-ordinates via the geom=(newdefinition) keyword. The fully nitrated dimer structure was used for MECH 1-2. For the mechanism involving protonation (MECH3), a hydronium cation was independently optimised to the same level. The dimer+cation complex was then optimised with and without CP correction for comparison. For the starting geometry of the intramolecular SN2 reaction (MECH4), the first ring of original dimer was manually adjusted to a boat conformation. Substituents were adjusted to appropriate axial and equatorial positions. All geometry scans were performed at 6-31+G(d) using either UB3LYP or ROB3LYP. Transition state searches were performed using UB3LYP/6-31+G(d). IRC calculations were performed using UB3LYP/6-31+G(d) and either the Hessian-based Predictor-Corrector (HPC), or the Euler integration predictor with the HPC corrector (EPC) algorithm.[46]

Following each successful scan, a low-level frequency calculation was performed on the obtained transition state. If singular imaginary vibration matching the key bond transformation for the reaction step persisted, then a transition state search was performed using this geometry. Where possible, the intermediate "product" geometry obtained from the successful scan was also optimised to B3LYP/6-311+G(d,p) for use in transition state searching using QST2 and QST3 methods.

3.4 Truncating the polymer model

obvs mention Shukla's studies here.

Looked at QTAIM for interaction with capping groups

[FIX ME]

The polymer structure was truncated to a dimer by Shukla et al. for the purposes of investigating the alkaline hydrolysis behaviour of NC.[3,4,35] Comparisons between the monomer, dimer and trimer found the dimeric structure to be the smallest suitable model for the chemical behaviour of the polymer. This is also observed when considering the minimum unit encompassing all bonding interactions necessary for parameterisation for a forcefield, for implementation in molecular dynamics simulations. The fully nitrated dimer structure used in this study consists of two non-planar β-D-glucopyranose rings joined by a glycosidic bond, with six nitrate groups attached at the 2,3,6 positions on each ring (Figure 11

The dimer ends are capped by methoxy groups rather than hydroxyl groups as were employed in Shukla's study. From the perspective of partial charges, and to an extent steric considerations, methoxy groups are expected to provide a better approximation for the ex-

tended polysaccharide.

Shukla's work identified the nitrate group attached to carbon three (C3) as the most susceptible to denitration and the first to be removed. This is supported by the distribution of partial charges in the molecule, with disregard of the capping groups. Thus, the nitrate group on C3 was used as the target site for degradation studies.

3.5 Summary

In this section

Chapter 4

Nitration Denitration Sequence of Nitrocellulose

4.1   Introduction

4.2   Computational details

All chemical species underwent an initial quantum mechanics (QM) geometry optimisation to the level of ωB97X-D / 6-31G(2df,p) and except where otherwise stated, were performed in Gaussian 09 D.01 (REF).

4.3   Results & Discussion

4.4   Summary

Chapter 5

Denitration Mechanisms

5.1 Introduction

Intro to the topic Stepwise denitration, peeling off, or alternative reactions dominate? Which in which conditions?

Camera's equations and most others agree that first stage of degradation in the presence of "spent" (?) acids involves hydrolysis, removing the nitrate group and forming the alcohol. [Here just reiterate the reactions you will be looking at. The actual literature should already have been covered in the lit review in the intro.]

5.2 Computational details

NC monomer and dimer structures underwent an initial molecular mechanics (MM) geometry optimisation using the COMPASSII forcefield(REF), performed in Materials Studio (version?). Subsequent QM geometry optimisations to the level of 6-31+g(2df,p) / wB9X-D, except where otherwise stated, were performed in Gaussian 09 D.01 (REF). [REMEMBER TO INCLUDE NMR AND FREQ OPTIONS I USED]

Programme, method (e.g. functional/ FF), settings(basis sets, thermostats, ensembles etc)

Include further calculation details - such as transition state theory etc, in another subsection (e.g. Transtion state theory) under this header.

Mention QTAIM if included in subsequent sections.

[FIX ME]

All electronic structure and reaction pathway calculations were implemented in GAUSSIAN 09 revision d01.43 Partial charges were obtained via PyRed (R.E.D. Server version 3.0).44,45 Molden 5.0.2 and Gaussview 5.0.8 packages were used for visualisation. To

circumvent the effects of BSSE, the largest computationally feasible basis sets are chosen and diffuse functions are included. A number of preliminary calculations were performed both with and without counterpoise correction (CP) to evaluate any inconsistencies. All studies were performed in the gaseous phase and initial structures were geometry optimised with B3LYP/6-311+G(d,p) and tight convergence criteria. Any incomplete or unconverged optimisations were restarted with generation of new internal co-ordinates via the geom=(newdefinition) keyword. The fully nitrated dimer structure was used for MECH 1-2. For the mechanism involving protonation (MECH3), a hydronium cation was independently optimised to the same level. The dimer+cation complex was then optimised with and without CP correction for comparison. For the starting geometry of the intramolecular SN2 reaction (MECH4), the first ring of original dimer was manually adjusted to a boat conformation. Substituents were adjusted to appropriate axial and equatorial positions. All geometry scans were performed at 6-31+G(d) using either UB3LYP or ROB3LYP. Transition state searches were performed using UB3LYP/6-31+G(d). IRC calculations were performed using UB3LYP/6-31+G(d) and either the Hessian-based Predictor-Corrector (HPC), or the Euler integration predictor with the HPC corrector (EPC) algorithm.[46]

Following each successful scan, a low-level frequency calculation was performed on the obtained transition state. If singular imaginary vibration matching the key bond transformation for the reaction step persisted, then a transition state search was performed using this geometry. Where possible, the intermediate "product" geometry obtained from the successful scan was also optimised to B3LYP/6-311+G(d,p) for use in transition state searching using QST2 and QST3 methods.

5.3　Truncating the polymer model

obvs mention Shukla's studies here.

Looked at QTAIM for interaction with capping groups

[FIX ME]

The polymer structure was truncated to a dimer by Shukla et al. for the purposes of investigating the alkaline hydrolysis behaviour of NC.[3,4,35] Comparisons between the monomer, dimer and trimer found the dimeric structure to be the smallest suitable model for the chemical behaviour of the polymer. This is also observed when considering the minimum unit encompassing all bonding interactions necessary for parameterisation for a forcefield, for implementation in molecular dynamics simulations. The fully nitrated dimer structure used

in this study consists of two non-planar β-D-glucopyranose rings joined by a glycosidic bond, with six nitrate groups attached at the 2,3,6 positions on each ring (Figure 11

The dimer ends are capped by methoxy groups rather than hydroxyl groups as were employed in Shukla's study. From the perspective of partial charges, and to an extent steric considerations, methoxy groups are expected to provide a better approximation for the extended polysaccharide.

Shukla's work identified the nitrate group attached to carbon three (C3) as the most susceptible to denitration and the first to be removed. This is supported by the distribution of partial charges in the molecule, with disregard of the capping groups. Thus, the nitrate group on C3 was used as the target site for degradation studies.

5.3.1 Denitration Sequence

Refer back to literature studies here.

How I picked which nitrate monomers to work with - just based on thermodynamics, and agreement with literature though, not experimental, or kinetic barrier work. But in the grand scheme of things, it doesn't matter too much, as I'd expect all to display a certain percentage of denitration / not being nitrated at all during synthesis (based on experimental evidence / fibre of the source cellulose etc) and the much more significant effect is how the post-denitration products go on to further react.

5.4 Thermal decomposition mechanisms

i.e not in acid Whilst the primary focus of this study is to explore the action of acids in the aging processes of NC , the thermolytic degradation routes must also be considered. These pathways are confluent with the reactions in the acid hydrolysis pathway and will dominate at elevated temperatures, due to their intramolecular character and therefore rapid, nature.

5.4.1 Homolytic fission

Comment on how you did it for PETN first, as a tester (but put the results in the appendices?)

[FIX ME - this seems to be computational details stuff] A methyl nitrate tester molecule was used for preliminary homolytic fission calculations on an N-O ester linkage (MECH1) (Figure 13). The bonding distance between oxygen and nitrogen was increased by 0.1 Å for 20 steps, beyond the length expected for bond fission. The separation of N-O was scanned using ROB3LYP and UB3LYP/6-31+G(d). Both test cases presented good agreement with the expected reaction co-ordinate.

This process was then replicated for the dimer, where the distance between oxygen 22 (O22) and nitrogen 23 (N23) of the nitrate ester on carbon 3 (C3) was increased (Figure 12). [THE REST SEEMS TO BE SPIEL. the graphics were nice though so maybe keep those]

From results section:

The methyl nitrate tester molecule presented an example of a successful geometry scan. A clear energy maximum corresponding to an expected transition state, is followed by a drop, suggestive of an intermediate or reaction product (Figure 17). The energy profile was obtained even though the scans were not able to complete the specified 20 steps. The UB3LYP process failed at step 16, whereas the ROB3LYP continued to step 19. At these end points, the presented energy value is not accurate but here have been included for context. The unrestricted and restricted-open cases show good agreement and near identical results for the steps where convergence was reached (1 – 15).

The reaction co-ordinate for the NC dimer did not present such a positive result. Again, the energy value at the final scan step (step 23) in both cases is not to be taken as accurate, with only partial convergence reached. Both the unrestricted and restricted-open techniques exhibited consistent results for the steps that did converge (steps 1-22) (Figure 18). Despite the unfavourable increase in energy, the observed bond breaking and formation during the course of the scan aligned with that expected of the mechanism. Though the scans did not identify any transition states or intermediate products, inspection of the geometry as the scan progressed revealed crucial points during the evolution of bond order. As the NO2 group departed O22, a partial double bond formed between C3 and O22, at step 12 of the scan. The frequency calculation on this geometry revealed a single imaginary frequency of -135.01 cm-1, indicating a transition state. The attempt to optimise this using a TS search was not successful. Multiple IRC calculations with various step sizes and both the EPC and HPC algorithms were also unsuccessful.

5.4.2   Intramolecular elimination of HNO$_2$

[Fix all of this] It was expected that as O22 approached H44 the generated reaction-co-ordinate would exhibit the normal reactant $\rightarrow$ transition state $\rightarrow$ product pattern, followed by either an asymptotic increase in energy or termination of the geometry scan, when the two atoms became too close or collided. However, despite showing the correct bond rearrangements as the distance between the nitrate oxygen the α-hydrogen decreased, the PES diagram only presented a rapid increase in energy. Frequency calculations on steps 7, 9 and

10 did not reveal any states possessing a lone imaginary frequency. Of the negative vibrations observed, none were illustrative of a proton transfer. Decreasing the C-O bond did not reveal any information on the transition state for MECH2. The C-O bond order increased to a triple bond after four steps, at a bond distance of 1.138 Å, in the both restricted-open and unrestricted cases. The expected approach of the peripheral oxygen towards the α-hydrogen was observed to be negligible.

5.5   Acid hydrolysis mechanism

5.5.1   Protonation site

Make sure to refer to the study by Polášek, Tureček, 2000, where they compare the different protonation sites in methyl nitrate. The have tables of bond lengths for O-N, adn consider more angles than I have - this is a good idea. They also agree that the "bridging" site is more stable than the terminal site. They also compared [bond lengths] in B3LYP and MP2. Denitration vs peeling off reaction, based on protonation site - it may be that peeling off is more favourable, but doesn't lead to mixed level of nitration - you can explain this and take it into account. Just proceed with having explained this / full understanding on future considerations. Thermodynamic numbers (in table) Scans of water approaching NC with the H coming off

Can do a bit of Multiwfn QTAIM here to look at H bonding and Critical bonding points

[FIX THIS] In all cases, stabilisation of the dimer-hydronium complex was not successful. It was found that the hydrogen of the hydronium ion immediately moved towards the nearest oxygen on the nitrate group. Despite these setbacks, the results could still be used to compare the effectiveness of CP correction for our system. THINK ABOUT COUNTERPOISE CORRECTION FOR LATER CALCS.

5.5.2   Denitration by hydrolysis

Different DFT functionals and HF and MP2 (?) Scans of the nitrate leaving the protonated NC. 2D scans of the water donating proton and nitrate leaving. Can also mention the scans which don't have water in - just NO2 leaving.

5.5.2.1   Comparison of different methods

wb97x-d, restricted vs unrestricted - show their 2D gaussian scan. uwb97x-d/ 6-31+g*, couldn't complete due to computational limitations. Or perhaps this is more of an appendicies thing, dependnt on the rest of the work in this section.

5.6 *(Effects of acid concentration on the Degree of denitration) - Maybe sprout to another section*

Phase diagram of monomer and dimer of acid conc vs nitrocellulose conc, for the denitration direction AND the nitration direction. Denitration is more important to us here, but nitratio ties in more with the paper by Rafeev. Come up with a sequence for nitration and denitration. Comment on the effect of acid on the denitration / nitrations behaviour of NC.

5.6.1 *(Monomeric NC model)*

5.6.2 *(Dimeric NC model)*

5.7 Summary

Found that Homolytic fission faster than elimination of HNO2, but the latter is more likely at etc... same as for PETN Phase diagram shows that with the increase in acid concentration, the degree of substitution increases by some modelling factor

Chapter 6

Post-denitration reactions

6.1 Introduction

6.2 Computational details

6.3 Thermodynamics of Ethyl Nitrate reactions

For an in ital comparison of the methods you used, you could do a diagram like the one Kuklja did (kuja2014.pdf, page 89, fig 3.7). She also makes mention of the overestimation of activation barriers for pure DFT methods. Make sure you know the background surrounding this - why does this occur, and what is done to remedy it?

6.3.1 Radical mechanistic route

6.3.2 Ionic mechanistic route

6.4 Thermodynamics of Nitrocellulose Monomer

6.5 *(Kinetics of Ethyl Nitrate)*

6.5.1 Radical mechanistic route

6.5.2 Ionic mechanistic route

6.6 *(Kinetics of Nitrocellulose Monomer)*

6.7 Summary

Chapter 7

Conclusion and future work

7.1 Conclusion

7.2 Future Work

Appendix A

Supplementary Data

A.1   Energies of NC species with different capping groups

Extra data tables etc.

Appendix B

Working scripts

Analysis & working scripts.

Just literally copypasta.

Appendix C

Computational architecture

This is a description of the tools you used to make your thesis. It helps people make future documents, reminds you, and looks good.

(Tabulate some details about the architecture I used - bare bones and copied from their websites)

Slater (out of commission) Legion Grace Huygens 1 Hugyens 2 Myriad Hawk

Bibliography

[1] Manoj K. Shukla and Frances Hill. Theoretical investigation of reaction mechanisms of alkaline hydrolysis of 2,3,6-trinitro-β-d-glucopyranose as a monomer of nitrocellulose. *Structural Chemistry*, 23(6):1905–1920, apr 2012.