

Abbreviations

| | |
|--------------------------------------|---|
| %N | percentage nitrogen by mass |
| 2-NDPA | 2-Nitrodiphenylamine |
| AIMD | <i>ab initio</i> molecular dynamics |
| AO | atomic orbital |
| a.u. | atomic units |
| B3LYP | Becke, 3-parameter, Lee-Yang-Parr hybrid functional |
| BCP | bonding critical point |
| BSSE | basis set superposition error |
| CH₃/CH₃ | NC repeat unit with two –OCH ₃ capping groups |
| CH₃/OH | NC repeat unit with –OCH ₃ capping group on ring 1 and –OH group on ring 2 |
| OH/CH₃ | NC repeat unit with –OH capping group on ring 1 and –OCH ₃ group on ring 2 |
| CCP | cage critical point |
| CP | critical point |
| DFT | density functional theory |
| DFT-D | density functional theory with dispersion correction |
| DSC | differential scanning calorimetry |
| DOS | degree of substitution |

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|---------------|---|
| DPA | diphenylamine |
| EN | ethyl nitrate |
| ESP | electrostatic potential |
| G09 | Gaussian 09 revision E.01 |
| GGA | generalised gradient approximation |
| GM | genetically modified |
| GTO | Gaussian type orbitals |
| GView | Gauss View 5.0.8 |
| HF | Hartree-Fock |
| HMF | hydroxymethylfurfural |
| HOMO | highest occupied molecular orbital |
| IR | infra-red spectroscopy |
| KS-DFT | Kohn-Sham DFT |
| LDA | local density approximation |
| MD | molecular dynamics |
| MEP | minimum energy path |
| MM | molecular mechanics |
| MMFF94 | Merck molecular force field 94 |
| MO | molecular orbitals |
| MP2 | Møller–Plesset perturbation theory with second order correction |
| MW | molecular weight |
| NBO | natural bond orbital |
| NC | nitrocellulose |

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|-----------------------|---|
| NCP | nuclear critical point |
| NG | nitroglycerine |
| NMR | nuclear magnetic resonance spectroscopy |
| 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 |
| RESP | restrained electrostatic potential atomic partial charges |
| RHF | restricted HF |
| RMS | root mean square |
| ROHF | restricted-open HF |
| UHF | unrestricted HF |
| SB59 | 1,4-bis(ethylamino)-9,10-anthraquinone dye |
| SCF | self-consistent field |
| SEM | scanning electron microscopy |
| SMD | solvation model based on density |
| S_N2 | bi-molecular nucleophilic substitution reaction |
| STO | Slater type orbitals |
| TG | thermogravimetric analysis |
| TS | transition state |

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|----------------------------------|--|
| UFF | universal force field |
| UV | ultraviolet |
| UV-vis | ultraviolet–visible spectroscopy |
| vdW | van der Waals |
| ωB97X-D | ω B97X-D long-range corrected hybrid functional |
| ZPE | zero-point energy |

Chapter 1

Conclusion and future work

1.1 Conclusion

Since winning a medal at the World's Fair in London in 1862 as the first man-made plastic [1, 2], nitrocellulose (NC) has become a central component in the manufacturing of everyday items across a whole spectrum of critical applications, from kitchenware to rocket fuel [3]. As has been demonstrated by this study and the extensive years of research since its first discovery, the degradation behaviour of NC is multi-staged and subject to high variation. The interplay of thermal triggers, hydrolytic initiation, as well as other factors not discussed here such as ultraviolet (UV) [4, 5] and physical shock [6], are all subject to the unique composition of each sample; variation owed to its biological origins and preparation method. Adding to this, the ageing reactions that occur are at the mercy of the precise environmental conditions under which the NC is stored. The final result is that the true, exhaustive reaction scheme for full decomposition has remained elusive.

In this thesis, the degradation processes in NC were explored using computational methods to elucidate the dominant processes and key reactants involved in ambient ageing. In the first section, the polymeric structure of NC was introduced. Different sized truncations and capping group approximations for polymer chain endings were tested as models for the polysaccharide. This was achieved by inspection of the partial charges, electrostatic potential (ESP) and critical interaction points for monomeric, dimeric and trimeric β -glucopyranose structures. The dimer was found to be the minimum structure required to reproduce the full properties of NC within a repeat unit.

Methoxy and hydroxyl capping groups were compared; the methoxy groups provided a more sterically and chemically similar proxy for the extended polymer, following examination of charges and geometry dependent interactions. Comparison of the charge densities

and intramolecular interactions around the monomer and dimer revealed that the former exhibited an acceptable level of deviation from the dimer behaviour, particularly with reference to further investigations concentrating only on localised reaction interactions. The bi-methoxy monomer was implemented as the model for NC in later studies.

Using the monomer model, the primary steps of decomposition were explored in Chapter ???. Thermolytic denitration reactions were investigated; homolytic fission of the nitrate O–NO₂ bond, and elimination of HNO₂ were tested for both the PETN test case, and the NC monomer model. Good agreement with literature values was found for the reaction energies and activation energies, in case of HNO₂ elimination in both pentaerythritol tetranitrate (PETN) and NC. The loss of •NO₂ *via* homolysis was confirmed. For the acid hydrolysis pathway, possible protonation sites in the monomer were analysed. It was found that the proton site most amenable to denitration was the bridging oxygen position of the nitrate. Further investigations considered denitration routes beginning from isomers protonated at both the terminal (upper) and bridging sites. The denitration step was then explored *via* a series of potential energy surface (PES) scans. The stability of different possible transition state (TS) ring structures involving both pre-protonation and concerted protonation-denitration was examined, in addition to the nature of the NO₂ leaving group. No stable TS structures presenting the correct vibration for denitration were isolated, however scans confirmed that the NO₂ was released as NO₂⁺, with possible formation of HNO₂ at greater separations.

Proposed decomposition routes originating from the primary denitration step were collated from nitrate ester reactions in literature. Using ethyl nitrate (EN) as an initial test case, the energies of each reaction were evaluated to determine whether it were a viable secondary reaction step following liberation of the •NO₂, NO₂⁺ or HNO₂ following first stage decomposition. Possible decomposition schemes were constructed, mapping from the point of NO₂ liberation to the oxidation of the alcohol group. The reaction energies were determined for the NC monomer. It was found that the energies were largely favourable from a thermodynamic equilibrium perspective. The fate of the released nitrogen species was in the accumulation of N₂O or regeneration of •NO₂, suggesting •NO₂ as the species responsible for autocatalytic processes in the system. Consumption of •NO₂ in the formation of acids proved to be thermodynamically unfavourable. HNO₂ routes lead to the formation of N₂O without self-regeneration and HNO₃ routes lead primarily to formation of •NO₂. This

indicates that HNO_2 was unlikely to be a direct contributor to catalysis, and that HNO_3 was the precursor to the $\cdot\text{NO}_2$ catalytic species, acknowledging experimental observations that HNO_3 appeared to facilitate autocatalysis [7].

Following the successful application of the monomer model in the investigation of denitration and protonation reactions of NC, further studies repeating the mechanisms explored here using the dimer (and trimer models, where feasible) would be extremely valuable. Possible synergistic effects of neighbouring nitrate groups on adjacent rings, in addition to increased steric factors, are likely to change the energetics and favourability of attack and protonation sites, thus altering the likelihood of denitration at each ring position. Inter-chain hydrogen bonding, largely dependent on unsubstituted hydroxyl groups, is also likely to alter the contribution to hydrolysis in particular. Porosity to solvents is influenced by local crystallinity and packing [8], and is sensitive to the spatial arrangements of individual hydroxyl groups [9, 10, 11]. Molecular packing will determine the ease at which liberated degradation products can diffuse through and escape the NC matrix. It can be surmised that there exists certain decomposition pathways with corresponding reactions that are solely structure dependent.

Whilst this work has not exhaustively explored the myriad reactions that may occur in the complex ageing procedures of NC, it has established the key reactions of the early stages of degradation, with presentation of an effective truncation of the polymeric structure applicable for further study in the topic. Key competing reactions for the denitration step, the identity of nitrogen species released and their role in the longer-range decomposition process has been presented. The conclusion of this project sets the scope for subsequent investigations into the later-stage reaction processes that lead to deeper degradation of the NC backbone.

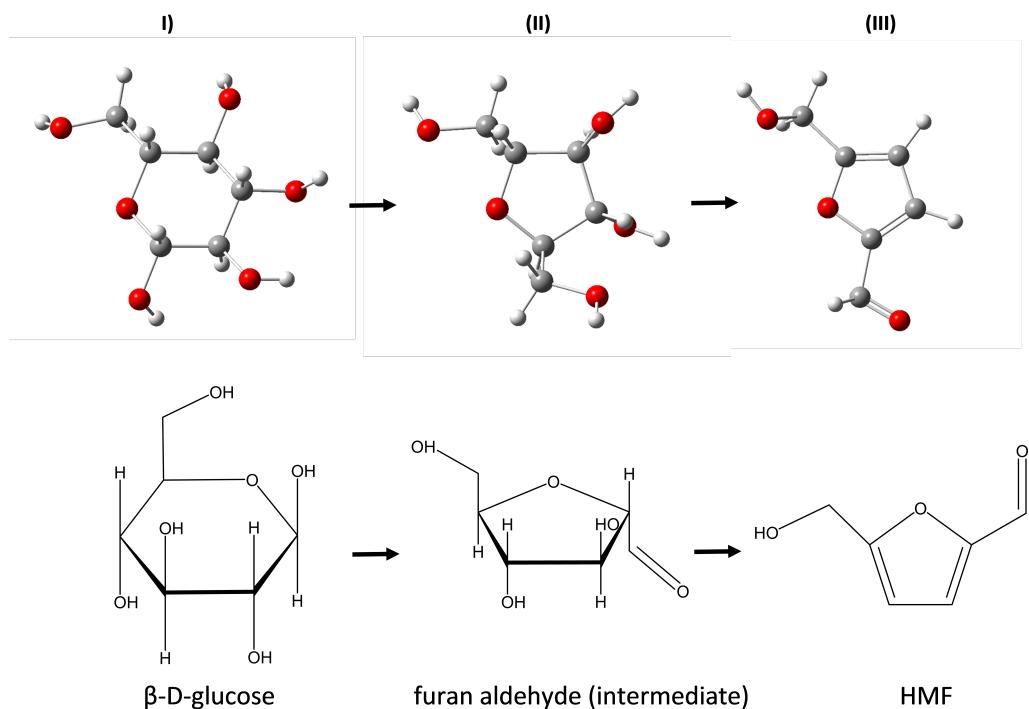
1.2 Further Work

In addition to expansion of the NC model to larger dimer and trimer units, the existing NC model may be refined by conducting a more rigorous examination of the subtle variations in geometry. Conformational scans, in particular for the C6 chain and for the orientation of the rings within the trimer, would benefit identification of other low energy structures likely to be present in the natural polymer. Here, only the denitration schemes for the singly nitrated NC monomer were documented. The differing stabilities of NC at varying levels of nitration will undoubtedly affect the reactivity at each site. Propagation of different nitration

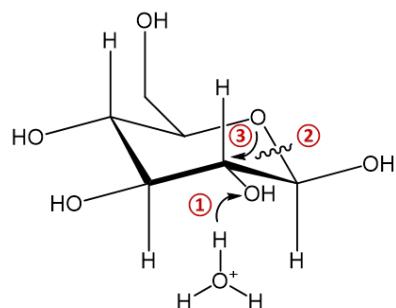
level and conformational structures through the denitration and secondary decomposition schemes may reveal alternative reactions, or alter the balance of products obtained.

Figure 1.1: The conversion of glucose to hydroxymethylfurfural (HMF) with a) showing the proposed reaction scheme, and b) displaying a possible mechanistic pathway, from the *ab initio* molecular dynamics (AIMD) study by Qian *et al.* [12].

(a) Conversion of glucose (I) to HMF (III) *via* a furan aldehyde intermediate (II).



(b) (1): Protonation of C2–OH on β-D-glucose, (2): breakage of the C2–O2 Bond, (3): the formation of the C2–O5 bond during glucose conversion to HMF.



Classical molecular dynamics (MD) techniques would also provide further insight into the diffusion of the released products, and their interaction with the wider polymer. Studies involving the interaction of NC with plasticisers has effectively probed the diffusion rates

of plasticiser migration, which is of key interest in the preservation of stable NC product formulations [?].

Another avenue of interest is in the exploration of other transition structures for the denitration stage, and for further degradation following formation of the ketone. The inclusion of additional explicit water molecules or water clusters may stabilise TS that were previously not viable, starting with reproduction of those for [?]. Ab-initio molecular dynamics (AIMD) techniques may be effective for the elucidation of water and acid interactions with NC, probing protonation behaviour and water clustering around monomer, dimer and trimer structures at different degree of substitution (DOS) [?].

A natural extension to the study of the secondary reactions driving decomposition is the expansion to a wider range of possible reaction pathways. These may include the widely documented mechanisms studied for glucose, such as the conversion to hydroxymethylfurfural (HMF), whereby the 6-membered ring is converted to a 5-membered ring (figure 1.1) [13, 14, 15]; furan and other aromatic species have been observed in NC degradation residues [16]. This is in addition to further studies of possible ring opening mechanisms and chain scission reactions, in order to fully account for the broad spectrum of experimentally observed degradation products in infra-red spectroscopy (IR) and nuclear magnetic resonance spectroscopy (NMR) measurements [?, ?, ?, ?, ?].

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