

# Chapter 1

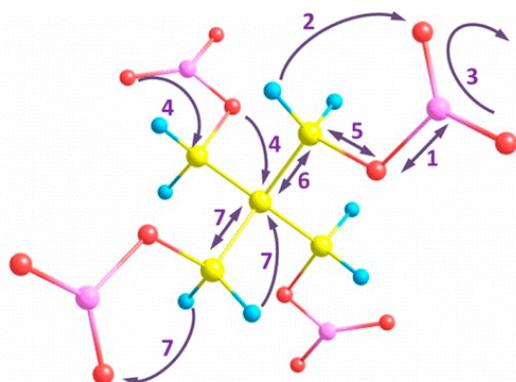
## Mechanisms of denitration

### 1.1 Introduction

The first stage of thermolytic decomposition for nitrate esters is generally agreed to be homolytic fission of the O-N bond linking the nitrate to the alkyl chain, leading to the loss of  $\cdot\text{NO}_2$  (equation 1.1) [?, ?, ?] Though nitrate homolysis is an endothermic reaction, the weak O-N bond has a typical dissociation enthalpy of 42 kcal mol<sup>-1</sup> and is easily cleaved when exposed to elevated temperatures, UV light or impact. Whilst the thermolytic degradation of energetic materials has been widely studied experimentally, the ambient, slow ageing mechanisms are less well documented. Low-temperature decomposition routes are influenced by many factors over a protracted lifetime, and in practical use, materials are usually subject to evolving environmental conditions. External changes in pressure, humidity, stress and temperature cycles induce variation in the degradation patterns of energetic materials. The presence of moisture has been observed to lower the activation energy and accelerate the decomposition of energetic materials [?]. Internal factors including impurities and residual solvent, and crystal growth within the bulk, also alter decomposition behaviour. It was found that the two dominating decomposition reactions were homolysis (equation 1.1) and intramolecular elimination of HNO<sub>2</sub> (equation 1.2). The decomposition of nitrate esters at temperatures over 100°C is dominated by thermolytic processes, whilst under 100°C, decomposition is thought to largely be the result of hydrolysis [?]. Tsyshevsky *et al.* studied the intramolecular reactions leading to denitration in PETN! in both the vacuum and the bulk crystal [?] (figure 1.1). Seven mechanisms for the removal of NO2! (NO2!) were



1.  $\cdot\text{NO}_2$  loss
2.  $\text{HNO}_2$  loss
3. OONO rearrangement
4.  $\gamma$ -attack
5.  $\text{ONO}_2^\cdot$  loss
6. C–C cleavage ( $\text{CH}_2\text{O} + \text{NO}_2$ )
7. C–C cleavage ( $\text{CO} + \text{HNO}_2$ )



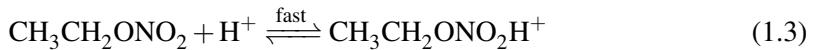
**Figure 1.1:** Intramolecular thermolytic reactions in PETN! (PETN!), from the work of Tsyshevsky *et al.* [?].

explored, corresponding to the labels in figure 1.1: (1) homolytic cleavage of the O–NO<sub>2</sub> bond, (2) the elimination of nitrous acid (HNO<sub>2</sub>), which is usually considered a competing reaction to homolytic fission, (3) the nitro-peroxynitrite rearrangement (O–ONO), (4)  $\gamma$ -attack of the terminating nitrate oxygen atom and the bridging nitrate oxygen at their relative  $\gamma$ -carbon sites, (5) the homolytic C–O bond cleavage, (6) and (7) two variations of the homolytic C–C bond cleavage. Whilst elimination of HNO<sub>2</sub> was found to be the most energetically favourable denitration pathway, homolytic fission dominated preliminary decomposition steps due to the lower activation barrier and faster rate of reaction. It was suggested that global decomposition processes were determined by the interplay between the two mechanisms. Initial homolysis facilitated wide-spread denitration, complemented by exothermic HNO<sub>2</sub> elimination promoting self-heating of the system and further bond dissociations. The presence of  $\cdot\text{NO}_2$  and HNO<sub>2</sub> were previously linked to autocatalytic rates observed for later-stage decomposition of nitrate esters [?, ?, ?, ?], though some studies solely attribute it to the presence of acids [?, ?, ?, ?]. However, from these initial processes it is not possible to determine which is the species responsible

Spent acids remain in the NC! (NC!) matrix following synthesis even with thorough washing procedures. Acids are further generated via the subsequent reactions of  $\cdot\text{NO}_2$  following homolysis. The acidic species proceed to react with other moieties in the system, such as unsubstituted alcohol side chains on the polysaccharide, or other small molecules free in the bulk.

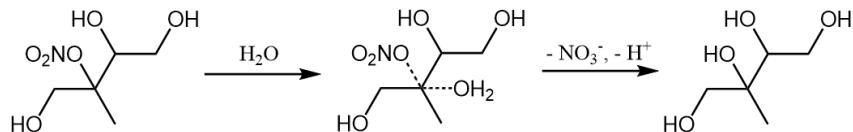
When exploring the interaction of nitroglycerol and nitroglycerin in acid solution, Cam-

era proposed a protonation-denitration scheme whereby initial protonation at the nitrate is rapid, but subsequent release of the nitronium ion was slow (scheme 1.1).



**Scheme 1.1:** The relative rate of stepwise protonation and denitration of nitrate esters, using ethyl nitrate as an example. From the work of Camera *et al.* [?].

NC! in storage is kept wetted with solvents to prevent drying and self-ignition. Material with 12.6pN! or lower, must be stored in 25% water by mass, or a mixture of solvents and plasticisers. In the study of organonitrates and organosulfates generated from isoprene as secondary organic aerosols, Hu *et al.* found that primary and secondary nitrates were resilient to hydrolysis for pH > 0, whilst tertiary nitrates underwent hydrolytic nucleophilic substitution easily, reacting with water to form alcohols [?]. In tertiary nitrates, the carbon



**Scheme 1.2:** Hydrolysis of a tertiary nitrate derived from the reaction of isoprene in the aerosol phase, from the work of Hu *et al.* [?].

is fully substituted with no attached hydrogens. This group is usually sterically hindered and stabilising to carbocations, condition on the other substituents. If formation of a carbocation intermediate is involved in the hydrolysis mechanism, this may explain why the tertiary nitrates exhibited highly efficient denitration, even under neutral conditions.

Though no specific mechanistic detail is given, the action of a protonated transition state during hydrolysis is alluded to by Hu *et al.*, through the contrast between the rate of acid-catalysed and neutral hydrolysis reactions. Neutral hydrolysis of the tertiary nitrates occurred rapidly, but hydrolysis only occurred for primary and secondary nitrates under strongly acid catalysing conditions at much lower rate. It was found that the presence of adjacent OH groups hampered the rate of hydrolysis for some aerosol dispersed organonitrates. In the neutral hydrolysis of tertiary nitrates, increasing the number of adjacent OH groups lead to protracted hydrolysis lifetimes. Interestingly, the retardation effect of adjacent OH groups was not observed for the acid catalysed cases. Hu proposed that this

could be due to the interaction of OH with the transition state of the neutral hydrolysis system, compared to the protonated transition state of the acid catalysed system, impeding the reaction only in the former case. There is evidence that nitration and denitration of nitrate esters is also influenced by the presence of nitrate groups at neighbouring positions. Matveev *et al.* demonstrated that for poly-nitroesters the rate of liquid-phase decomposition did not increase linearly with number of nitrate reaction centres. It was found to mainly dependend on individual structures (table 1.3) [?].

It was suggested that the trend in reactivity could be partially explained by the inductive effect of the nitro groups [?]. The inductive effect arises when a difference in the electronegativity between atoms connected by a  $\sigma$  bond leads to a polarisation, or permanent dipole, in the bond. Electron donating groups increase the  $\delta-$  partial charge on neighbouring atoms through the release of electrons, whilst electron withdrawing groups pull electron density away from neighbouring atoms generating a  $\delta+$  charge on connected atoms. However, the  $\pi$  donation by lone pairs on the oxygen and nitrogen plays a significant role in increasing electron density of neighbouring atoms, known as the resonance effect.  $\text{NO}_3$  presents a stronger electron donating effect via  $\pi$  donation than OH. It would therefore be expected that both increase the rate of hydrolysis for nearby leaving groups. The presence of an adjacent nitrate appears to facilitate denitration, whereas the presence of hydroxyl groups hinders this process, for neutral hydrolytic schemes. This suggests that the proposed interaction of the

**Table 1.1:** Comparison of rate constants of decomposition for various polynitrate esters at 140°C. Collated from literature sources by Matveev *et al.*[?].  $\Delta T$  is the decomposition temperature range,  $E$  is the experimental activation barrier for decomposition,  $\log A$  is the pre-exponential factor,  $T_c$  is the combustion temperature,  $k_{\text{expt}}$  is the rate constant for decomposition.

Compound	$\Delta T$ / °C	$E$ / kcal mol <sup>-1</sup>	$\log A$ [s <sup>-1</sup> ]	$k_{\text{expt}}$ / 10 <sup>-6</sup> s <sup>-1</sup>
$\text{O}_2\text{NOCH}_2\text{CH}_2\text{CH}_2\text{ONO}_2$	72–140	39.1	14.9	1.7
$\text{O}_2\text{NOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{ONO}_2$	100–140	39.0	14.7	1.1
$\text{O}_2\text{NOCH}(\text{CH}_3)\text{CH}(\text{CH}_3)\text{ONO}_2$	72–140	40.3	14.9	5.0
$\text{O}_2\text{NOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{ONO}_2$	80–140	42.0	16.5	1.9
$\text{O}_2\text{NOCH}_2\text{CH(OH)}(\text{CH}_2\text{ONO}_2)$	80–140	42.4	16.8	2.3
$\text{O}_2\text{NOCH}_2\text{CH(ONO}_2)(\text{CH}_3)$	72–140	40.3	15.8	3.0
$[(\text{O}_2\text{NOCH}_2)\text{CH(ONO}_2)\text{CH(ONO}_2)]_2$ (hexanitromannite)	80–140	38.0	15.9	63.0

hydroxyl group with the neutral transition state supersedes its resonance effect. As a result, it is ambiguous whether any apparent rate increase due to the presence of adjacent nitrate groups arises as a result of the resonance effect of the nitrate, or whether it is solely due to the absence of a neighbouring hydroxyl.

The investigation by Hu *et al.* exclusively focused on nitrates generated from an isoprene precursor, upon dispersion as an aerosol. The nitrate groups present in NC! are either of primary (C6) or secondary (C2, C3) structure, indicating that ambient hydrolysis is unlikely according to this scheme. However, solvent effects are expected to differ for condensed-phase reactions and aerosol phases. A greater build-up of acid concentration can be achieved in a closed, condensed system, and the lifetime of an aerosol is relatively short-lived when considering the timescale of slow ageing processes in NC!. Thus, the work of Hu *et al.* does not provide a direct comparison for the NC! polymer but highlights the the possible contribution from both neutral and acid-catalysed hydrolysis routes and of increasing levels of substitution on the wider structure.

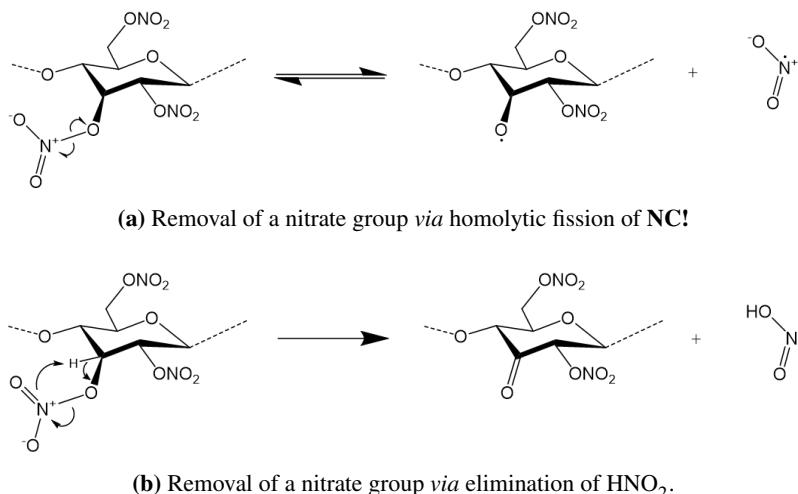
In this section, the possible mechanisms for nitrate removal from the NC! backbone are explored. The homolytic fission and HNO<sub>2</sub> elimination thermolytic processes suggested by Tsyshevsky will be compared to the acid hydrolysis scheme. Though the relative rates of reaction were not compared, the extended timescales involved in ambient ageing imply that the dominating reactions correspond to those most thermodynamically favourable.

## 1.2 Methodology

The energies of homolytic fission and elimination of HNO<sub>2</sub> were calculated for PETN, as a test system before extension to the monomer. The reaction energies were calculated according to equations 1.1 and 1.2 to reproduce the work of Tsyshevsky *et al.*. The literature geometries of PETN and its derivatives were obtained from the authors. A single point energy and frequency calculation were performed on each of the relevant structures to determine the reaction energies; no geometry optimisation was performed on the given structures except for in the case the 'NO<sub>2</sub> molecule, where the geometry was not given.

The intramolecular reactions of the NC! monomer were modelled according to scheme 1.3. Rigid and relaxed PES! (PES!) scans were attempted in order to locate transition states for both reactions for the NC! monomer. Where the scans were unable to identify a valid transition state geometry, guess transition state geometries were constructed and optimised.

The possible protonation sites for the NC! monomer were explored by placing a proton



**Scheme 1.3:** The proposed intramolecular reactions for the initial denitration step during NC! degradation.

at each of the different oxygen sites surrounding the nitrate group. The structures were then geometry optimised and energies of protonation were compared. H<sub>3</sub>O<sup>+</sup> was modelled as the donating species; as NC! is usually stored wetted in water, the hydronium ion is the most likely source of protons. It is also possible that the proton is donated by other acidic species in the system, particularly HNO<sub>2</sub> or HNO<sub>3</sub>. This is more likely at later stages of degradation when a higher concentration of acid has been generated by secondary reactions. The effects of tunneling were not accounted for.

### 1.2.1 Computational details

All geometry optimisation, thermochemistry calculations and PES! scans were performed in **G09!** (**G09!**). Geometry optimisation and thermal calculations were to the level of 6-31+G(2df,p). NC! monomer structures were optimised using **wb97xd!** (**wb97xd!**), **B3LYP!** (**B3LYP!**) and **MP2!** (**MP2!**). ΔG values were obtained by the difference between the thermally corrected free energies of products and reactants. Zero-point corrected energies **ZPE!** were determined by addition of individual **ZPE!** (**ZPE!**) to the free energy:

$$\Delta G^{ZPE} = \sum(G_{products} + ZPE_{products}) - \sum(G_{reactants} + ZPE_{reactants}) \quad (1.5)$$

PES! scans were performed to the level of **wb97xd!/6-31+g(d)**, or using unrestricted **wb97xd!**, in the case of O-NO<sub>2</sub> dissociation. Rigid scans were carried out by fixing bond lengths, angles and dihedral values as constants. Only the variable of interest was allowed to change, with the exception of relaxation of other specified coordinates required

for accommodation of the new geometry, following each step of the scan. For example, in the homolysis of the nitrate O–NO<sub>2</sub> bond, as the NO<sub>2</sub> group departed, the internal O–N–O angle was also allowed to relax, in addition to the angle of the departing NO<sub>2</sub> with respect to the remainder of the molecule. In two-dimensional scans, two variables are scanned. For the same reaction, the elongation of a the O–NO<sub>2</sub> bond was scanned with simultaneous approach of a proton, to monitor the effect of protonation for the same reaction. Relaxed scans were performed in Gaussian using the ‘modredundant’ function, whereby the whole structure was geometry optimised after each step of the scan. Scans were performed with step size of 0.1 Å. The number of steps varied with the property investigated, though the majority of the phenomena were observed within 20 steps (2 Å). Scans were attempted in vacuum, and for some cases, **PCM!** (**PCM!**) implicit solvent [?].

## 1.3 Results and discussion

### 1.3.1 Thermolytic decomposition mechanisms

The energies of homolytic fission and intramolecular elimination of HNO<sub>2</sub> from a **PETN!** nitrate group are shown in table 1.2. The energy values calculated by Tsyshevsky *et al.* are denoted in parenthesis. Despite using the supplied geometries, same method and basis, it

**Table 1.2:** Calculated free energies of reaction ( $\Delta G_r$ ), reaction enthalpies ( $\Delta H_r$ ), activation barriers ( $E_a$ ) with zero-point correction ( $ZPE$ ) for the intramolecular reactions of PETN, and the **NC!** monomer. Values expressed in kCal mol<sup>-1</sup>.

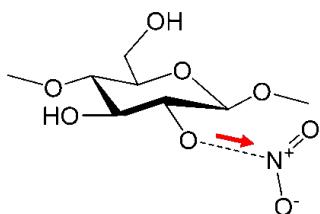
Reaction	$\Delta G_r$	$\Delta G_r^{ZPE}$	$\Delta H_r$	$E_a$	$E_a^{ZPE}$
<b>PETN</b>					
·NO <sub>2</sub> loss	21.51 (41.2) <sup>a</sup>	16.56 (35.8)	35.62	21.5 <sup>b</sup> (41.2)	16.56 (35.8)
HNO <sub>2</sub> loss	−23.63 (−18.6)	−26.21	−20.39	41.29 (47.3)	36.28 (42.7)
<b>NC!</b> monomer					
·NO <sub>2</sub> loss	23.25	18.69	36.26	23.25	18.69
HNO <sub>2</sub> loss	−36.05	−39.42	−22.86	40.70	37.33

<sup>a</sup> values from the work of Tsyshevsky *et al.* [?].

<sup>b</sup> values for the activation energy and total energy of reaction are the same for bond dissociation via homolytic fission.

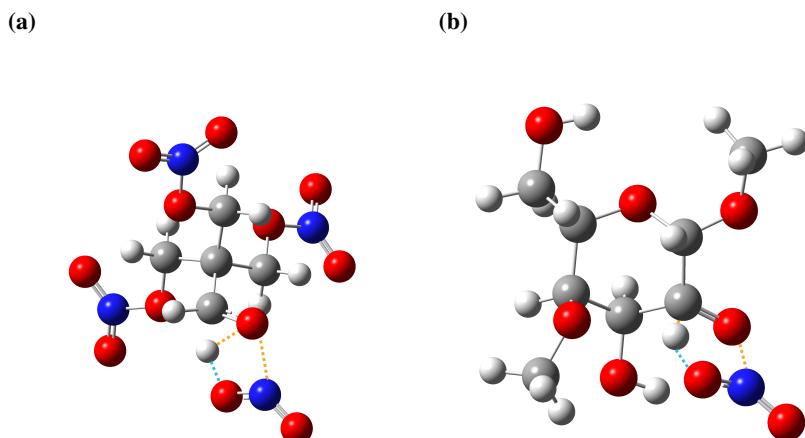
can be seen that the obtained PETN reaction energy in the case of homolytic fission varies greatly from the value found by Tsyshevsky *et al.*. Inspection of the forces for the given

structures showed that they were in fact not converged, however it was expected that the supplied geometries were used to generate the reaction energy values quoted in the study. The un converged structures therefore do not fully explain the large discrepancy between the literature energies and obtained values here. A contribution may arise from a different compilation of the **G09!** program, leading to fluctuations in the exact values obtained which are amplified when deriving reaction energies, though these are not expected to account for the 20 kCal mol<sup>-1</sup> deficiency in the homolysis reaction energy.



**Figure 1.2:** The O–NO<sub>2</sub> bond was elongated during rigid and relaxed **PES!** scan to simulate homolytic fission for the **NC!** monomer.

The energy profile of homolytic fission was obtained via **PES!** scans of NO<sub>2</sub> leaving the **NC!** monomer (figure 1.2). The internal angle of the departing NO<sub>2</sub> was allowed to relax, in addition to the coordinates referencing its orientation relative to the rest of the molecule. As the scan progressed, the NO<sub>2</sub> internal angle increased from 129.2 ° to 134.0 ° at a maximum separation of 3.4 Å from the bridging oxygen (Ox). This corresponds to the literature value for the O–N–O internal angle 134.3 °) and confirms the formation of a 'NO<sub>2</sub> radical. The values obtained for HNO<sub>2</sub> elimination of PETN match the results given by Tsyshevsky much more closely. The energies fall within 5 kCal mol<sup>-1</sup> and 6 kCal mol<sup>-1</sup> for the Gibbs free energy of reaction and activation barrier, respectively. This is within a reasonable margin of error for comparing with experimentally obtained values, though larger than expected for those derived using the same method, basis and structure. In the case of the **NC!** monomer, both rigid and relaxed scans failed to capture the **TS!** (**TS!**) for cleavage of the nitrate group via interaction with the  $\alpha$ hydrogen. A guess transition state was constructed based on the **TS!** of the analogous reaction for PETN, and optimised to produce the structure of the correct imaginary vibration.

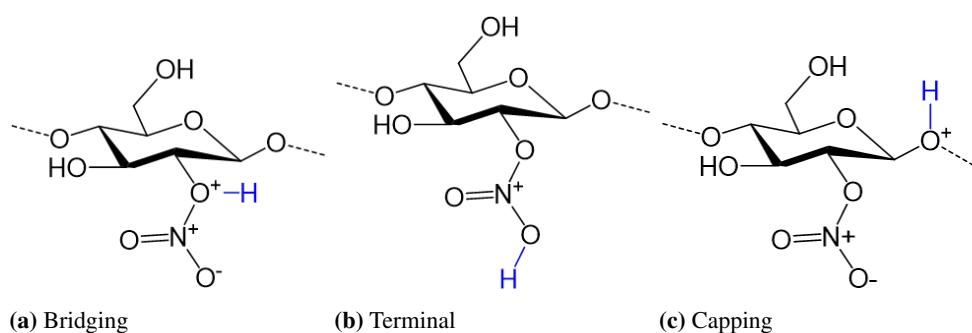


**Figure 1.3:** TS! for the elimination of  $\text{HNO}_2$  by removal of the  $\alpha$ -hydrogen by the  $\text{NO}_2$  leaving group in 1.3a PETN and 1.3b NC. Orange dashed lines indicate bonds breaking and blue dashed lines indicate bonds forming.

### 1.3.2 Acid hydrolysis mechanism

#### 1.3.2.1 Protonation site

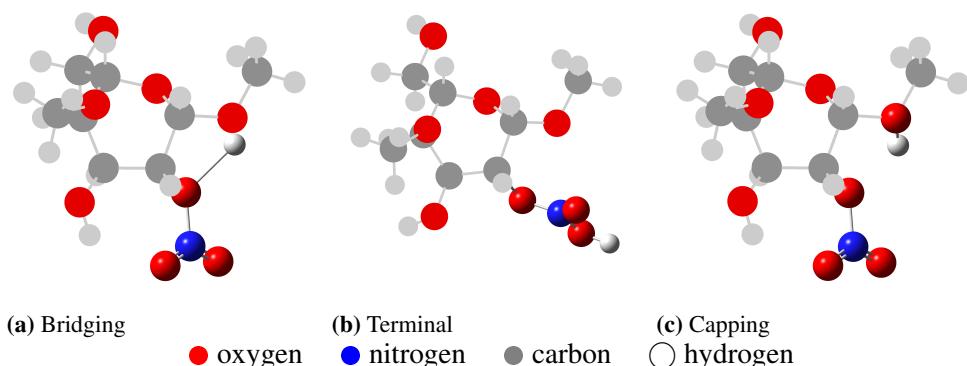
The protonated NC! monomer species are shown in figure 1.4. The bridging oxygen (Ox) linking the nitrate to the remainder of the molecule, the capping group oxygen, and the interchangeable terminal nitrate oxygen sites were protonated in order to compare their relative energies for determination the site most likely to stabilise the proton at thermal equilibrium. Protonation also occurs on other sites in the molecule, such as at unsubstituted hydroxyl oxygen sites, the capping group oxygen on C4 and O1 in the glucose ring. Though it is a possibility that protonation at further sites in the monomer would contribute to degradation, these processes would occur *via* alternative mechanisms without the involvement of denitration. For the purposes of studying acid hydrolysis, only the sites peripheral to the nitrate leaving group were explored. The mechanism of protonation was not explored in



**Figure 1.4:** Protonation sites on the NC! monomer for hydrolysis of the nitrate at the C2 position.

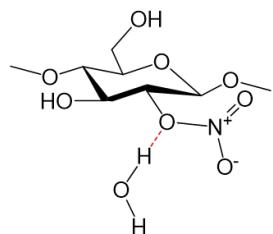
**Table 1.3:** Free energies of protonation at each of the oxygen sites of interest on CH<sub>3</sub>CH<sub>3</sub>! (CH<sub>3</sub>CH<sub>3</sub>!) C<sub>2</sub> monomer of NC!.

Protonation site	$\Delta G_f / \text{kcal mol}^{-1}$			
	wb97xd!	PCM	B3LYP!	PCM
Bridging	-30.88	0.85	-31.99	-0.25
Terminal	-23.13	10.00	-24.06	10.97
Capping	-30.43	0.85	-31.98	0.64



**Figure 1.5:** Optimised protonated NC! monomer structures, showing interaction between the proton on the bridging site with the capping group oxygen.

depth here; it was assumed that protons in the system would be in fast exchange between the molecule and the solvent. The process has been studied computationally by Jebber and Liu *et al.* [?, ?]. It can be seen that the bridging and capping values are very similar using both wb97xd! and B3LYP!. Inspection of the geometries reveal that the optimised bridging and capping structures are extremely similar (figures 1.4a and 1.4c). The difference in energies between the gaseous and implicit solvent values can be explained as H<sub>3</sub>O<sup>+</sup> is highly unstable in vacuum and prefers to lose the proton to exist as water, whereas when solvated, the positive charged is stabilised. Thus the energy gain from losing the proton is less pronounced when in solvent. Water as the protonating species was attempted, by

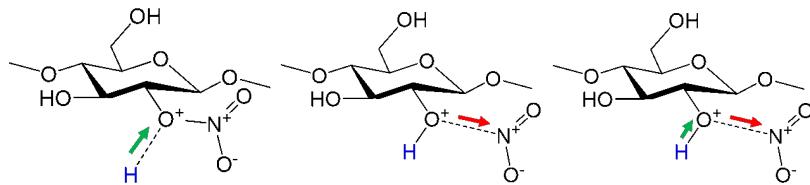


**Figure 1.6:** The attempted geometry of single water coordination to the monomer! (monomer!).

optimisation of one, two and three water molecules in coordination with the nitrate site in the **NC!** monomer, however no stable complex could be isolated. It is anticipated that a much larger network of waters around both the region surrounding the nitrate and the wider molecule would be required to achieve a stable water coordination in order for further investigation into the nature of neutral hydrolysis (figure ??). Evaluation of the energy of protonation at each site found that the bridging and capping sites most likely. However, all possible structures will be explored for the subsequent denitration stage.

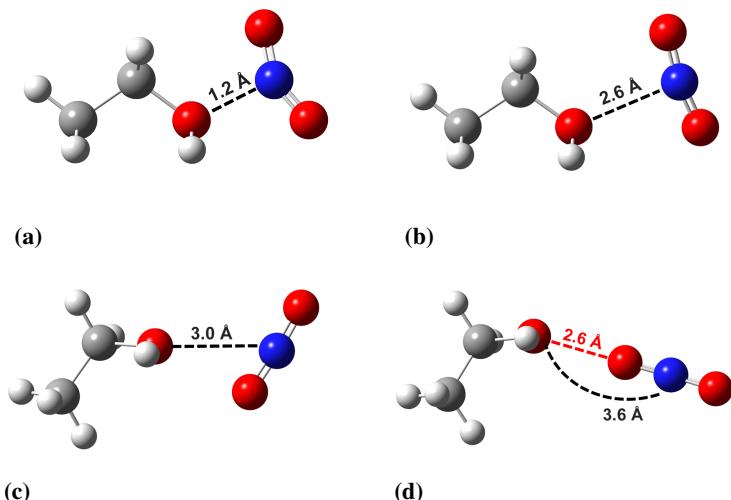
### 1.3.3 Denitration by hydrolysis

Following the protonation step, possible transition states for the removal of the nitrate were investigated. Direct dissociation of  $\text{NO}_2$  from the protonated species was explored, along with the simultaneous approach of a proton and cleavage of the  $\text{NO}_2$  (figure 1.7). The scan of the proton moving towards the bridging site was also completed to gain insight to the energy profile of the process. The relaxed **PES!** scan of  $\text{NO}_2$  removal from ethyl



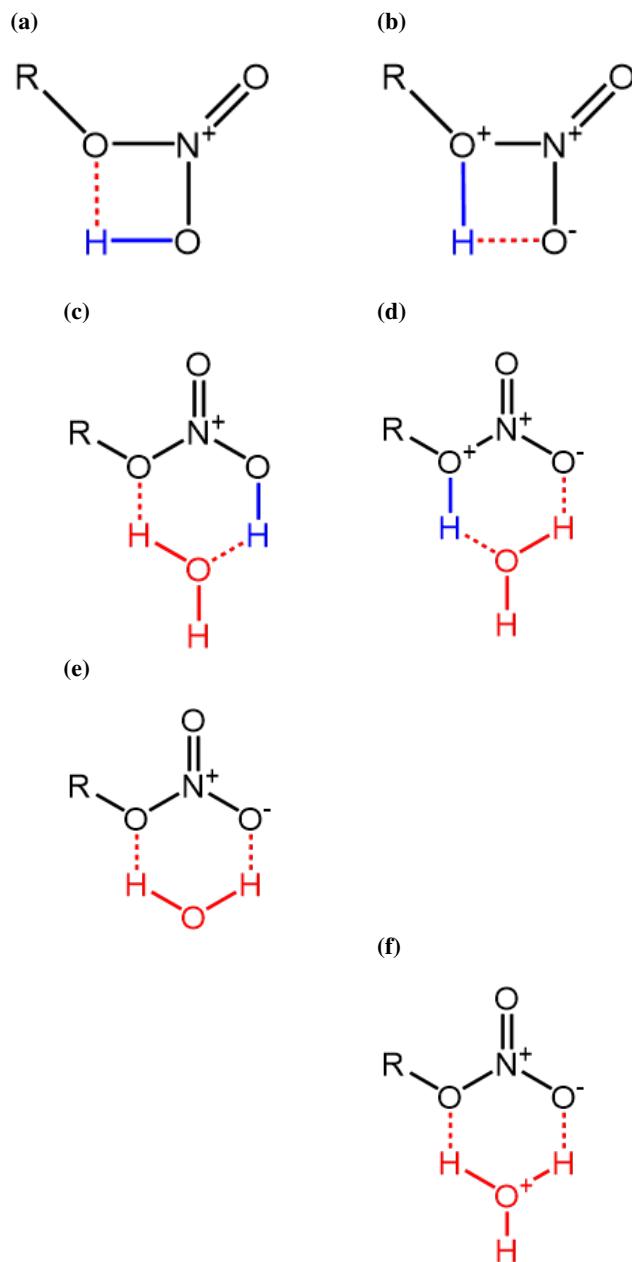
**Figure 1.7:** The scanned coordinates of ??) proton approach, ??) dissociation of  $\text{NO}_2$  and ??) concerted protonation and  $\text{NO}_2$  dissociation.

nitrate protonated at the bridging site was used as a preliminary test for the mechanism of denitration following protonation (figure 1.8). Unrestricted **wb97xd!** was used, with 20 steps of 0.1 Å, however bond dissociation was not illustrated in the energy profile even when extending the scan distance to a maximum of 6.4 Å. Instead, a steady increase in the energy was observed. It can be seen that as the nitrate departs, the whole molecule rotates and the  $\text{NO}_2$  leaving group aligns with the hydroxyl in an orientation suitable for formation of a peroxy group. The internal angle of the leaving group increases to 180 °, confirming that  $\text{NO}_2$  leaves as  $\text{NO}_2^+$ . This was the expected outcome for hydrolysis, as it is anticipated that the  $\text{NO}_2^+$  will further react to produce acids conducive to further hydrolysis. Proposed 4-membered ring and 6-membered ring **TS!** were investigated in order to determine whether they energetically and geometrically reasonable structures. Optimisations were attempted



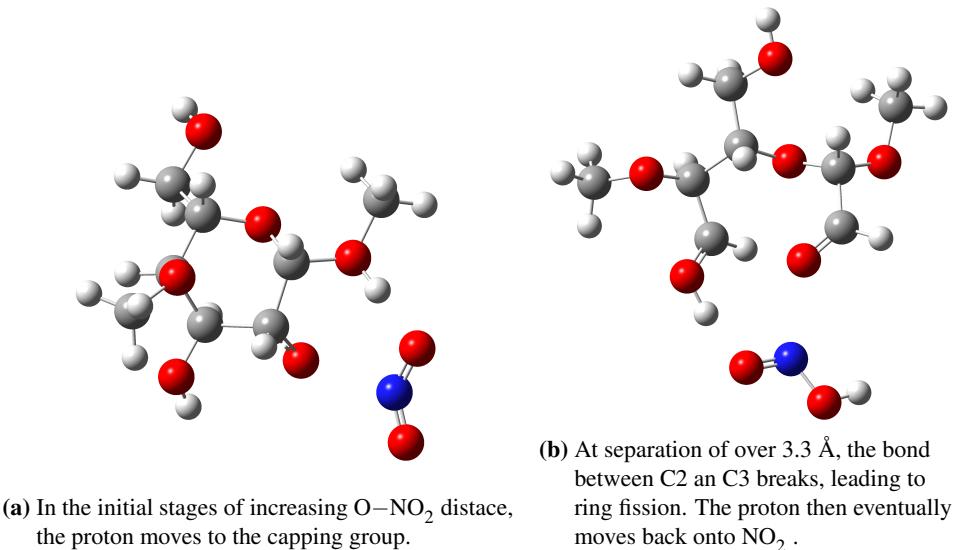
**Figure 1.8:** Geometries from steps 1, 7, 11 and 26 of the **PES!** scan of **EN!** (**EN!**)

with both full geometry relaxation, and various frozen coordinate schemes for each proposed **TS!**. The R groups were simplified to methyl nitrate ( $R = \text{CH}_3$ ) in effort to limit degrees of freedom during optimisation of the **TS!** structures, however no fully relaxed structures were able to achieve convergence. Fixing of the bulk molecule with relaxation only around the nitrate and coordinating species, or relaxation of the wider molecule with fixed coordinates around the nitrate, allowed sequential optimisation of different moieties, increasing chances of global energy minimisation. It was possible to optimise the 4-membered ring bridging **TS!** on the **NC!**monomer with frozen **TS!** ring geometry *via* preliminary optimisation of the ring structure with methyl nitrate. The optimised ring geometry was then placed on the monomer, with fixing of the coordinates, allowing the remainder of the molecule to relax. A rigid scan was then performed of the 4-membered ring transition starting from the bridging site protonated monomer. It was revealed that as the nitrate moved away from the system, the proton moved to the capping group site rather than remain on the bridging oxygen as a hydroxyl, as was expected. Instead, a ketone group was formed between the bridging oxygen and the ring. At subsequent steps, the ketone group causes the C2 - C3 bond to elongate and break. The scan eventually revealed the  $\text{NO}_2$  leaving group reclaiming the proton from the capping group oxygen, leading to ring fission. The activation and kinetic barrier involved in ring fission is much higher than that of denitration, so the product of the scan is likely due to the geometric constraints placed on the geometry of the departing  $\text{NO}_2$  group, rather than a physically energetic process. However, it sheds light on the scheme by which ring fission occurs, with has been implied in previous work involving the prior



**Figure 1.9:** Proposed 4-member and 6-member ring transition states for the denitration of a nitrate ester, under various hydrolytic conditions. R = CH<sub>3</sub> in the case of methyl nitrate, R = CH<sub>2</sub>CH<sub>3</sub> in the case of ethyl nitrate and R = (H<sub>3</sub>CO)<sub>2</sub>C<sub>6</sub>H<sub>9</sub>O<sub>3</sub> for the monomer.

formation of a ketone. Attempts to isolate the other **TS!** structures were unsuccessful, even



**Figure 1.10:** Relaxed scan of  $\text{NO}_2$  departure, starting with the 4-membered ring structure.

when simplifying the side chain to methyl nitrate and applying implicit solvent in the case it stabilised the charges on the strained structures.

## 1.4 Summary

Homolysis is fastest, for the monomer too, with  $\text{HNO}_2$  coming in second due to slower rate / energetics. (Check if I did anything to actually find this out - may just have to compare energetics.) Scans did confirm that ' $\text{NO}_2$ ' left as a radical. Scans showed the energy profiles involved (again, was  $\text{HNO}_2$  ever seen to be formed? )

AH rate was not able to be compared as a TS was not found. Protonation occurs on both terminal and bridging sites of the monomer, with location at the bridging site conducive to the removal of  $\text{NO}_2^+$ .

TS were not able to be isolated for the denitration step, even with coordination with water in different orientation and both 4 and 6 mem ring TS. 2D scans did reveal a possible TS but it did not lead to the desired denitration pathway. See water clusters around NC by [?].