

Chapter 4

Post-Denitration Reactions

[Fix the arrows of the reaction schemes? So that eluting products leave with a u shaped arrow?]

4.1 Introduction

Products of the preliminary denitration step of **NC!** (**NC!**) can be evolved as gases or remain trapped in the polymer matrix. Reactive nitrous oxide radicals generated from homolysis of the O-N bond are likely to migrate within the bulk and attack other sites on the polysaccharide. Nitrous and nitric acids released directly from denitration, or via transformation of released NO_x species, contribute to the acidity of the overall system, lowering the pH and stimulating further hydrolysis processes.

When studying the ageing of **NC!** using **UVVis!** spectroscopy, Moniruzzaman *et al.* observed increasing concentrations of secondary reaction products following heat treatment over extended timescales* (figure 4.1) [?, ?]. **UV!** absorbances at 600 nm and 650 nm were characteristic of the **SB59!** (**SB59!**) dye used to indicate the presence of NO_x , released by the denitration of **NC!**. The isosbestic point identified at 552 nm showed that as the concentration of **SB59!** decreased, the concentration of the [**SB59!** + **NC!**] product increased. For measurements $>40^\circ\text{C}$, the isosbestic point demonstrated a shift downwards. This was most clearly illustrated by the 70°C case, whereby the final measurement (indicated by the royal-blue line in bold) deviated from the isosbestic point entirely, and presented more than 81% consumption of the original dye concentration. The drift of the isosbestic point with the appearance of new peaks below 400 nm suggests the presence of additional species in the reaction mixture. It is likely that these arise from the continued reaction of **SB59!** derivatives with **NC!** degradation products, or further derivatives thereof, as suggested in

*First introduced in section ??

scheme 4.1.

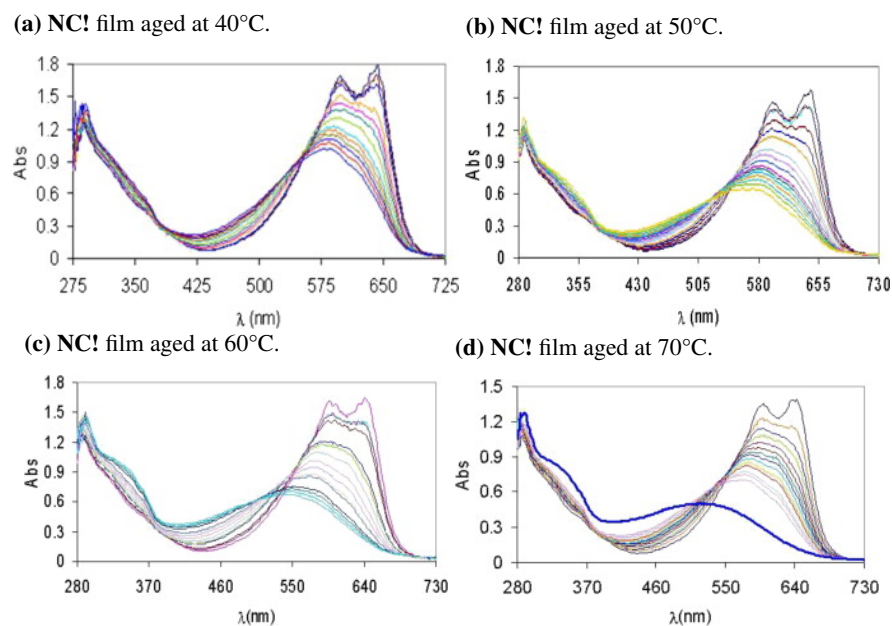
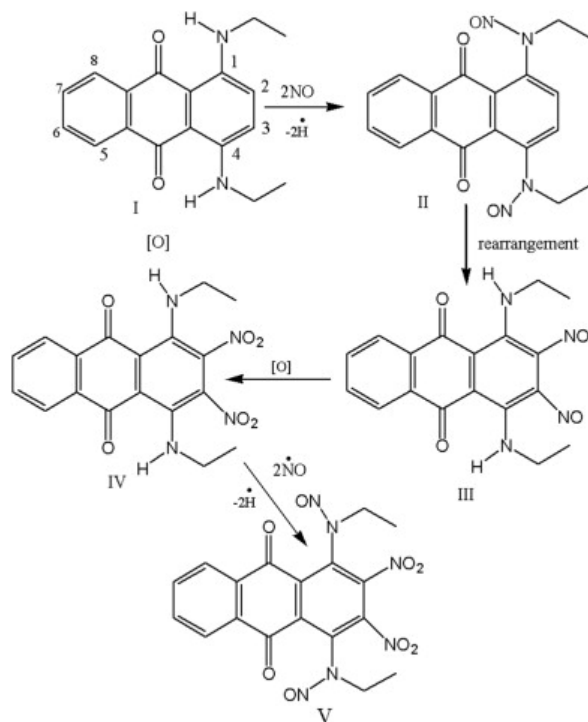


Figure 4.1: UVVis! spectra of aged NC!-based film, from the work of Moniruzzaman *et al.*[?]. The peaks at 600 nm and 650 nm are attributed to the $\pi - \pi^*$ transitions in the anthraquinone dye (SB59!). Spectral lines with highest absorbance in this region correspond to the sample prior to heat treatment. Peaks below 400 nm indicate the formation of SB59! derivatives due to secondary reactions.

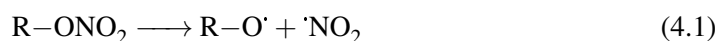


Scheme 4.1: Proposed reaction pathway for the the SB59! dye with NO_x released as a result of denitration of NC! [?].

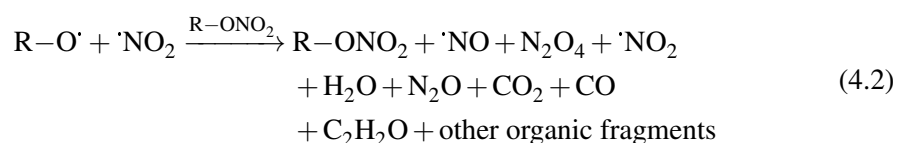
Following the possible denitration routes outlined in Chapter 3, the remaining residues are available for further reaction with the polymer or other free molecules in the system. Chin *et al.* proposed schemes for the propagation of such reactions initiated by both thermolysis and hydrolysis of nitrate esters [?]:

Thermolysis

Initiation:

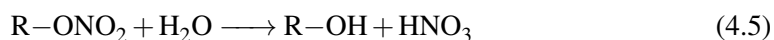


Propagation:

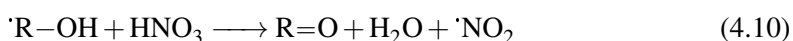
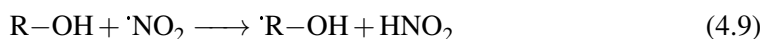
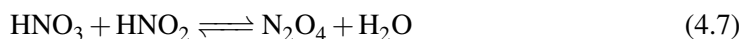


Hydrolysis

Initiation:

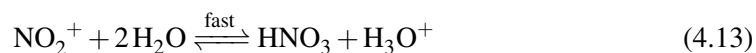
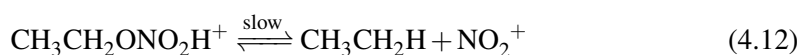


Propagation:



The hydrolysis equations were modified from an earlier work by Camera *et al.*, where the scheme was presented with ethyl nitrate (where $\text{R} = \text{CH}_3\text{CH}_2$ for the scheme above) [?]:

Hydrolysis

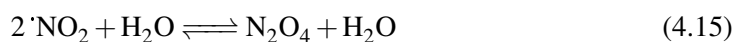
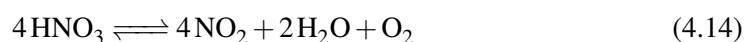


The oxidation of alcohol by nitric acid (equation 4.6) is slow, thus rate-limiting, and

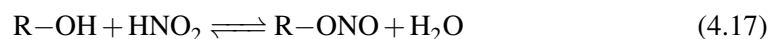
likely to occur *via* a series of intermediate reactions where the mechanism is not known. Following the generation of nitrous acid, subsequent oxidations occur rapidly. Equations 4.7 - 4.10 describe a possible branched radical chain mechanism, fed by the nitrous and nitric acids produced during the hydrolysis and alcohol oxidation reactions during the initiation stages. The reactions in the branched radical chain mechanism for thermomolysis are poorly characterised, only defined by the observable products. Termination reactions were not emphasised in the schemes, for these cases.

Aellig *et al.* presented an alternative scheme when determining the decomposition of benzyl nitrate ($\text{PhCH}_2\text{ONO}_2$, $\text{R} = \text{PhCH}_2$), involving more interaction with the solvent [?]:

Initiation



Propagation



Termination



However, for the initiation reactions Aellig prescribes the use of an amberlyst catalyst. The propagation reactions are acid catalysed by HNO_2 .

Both the Camera/Chin and Aellig schemes above produce final end products observed in the decomposition of **NC!**. In particular, Aellig's scheme accounts for the production of N_2O , which forms a XXXX part of the decomposition eluent.

It is widely agreed that first-stage decomposition follows a first-order process (or pseudo-first order, with respect to hydrolysis reactions). A number of studies observe catalytic rate of decay for the longer-term aging processes. Dauerman [?] observed that when **NC!** was treated with NO_2 gas before heating, the time required for sample ignition halved. He suggested that the NO_2 adsorbed onto the surface acted as a catalysing agent.

Neutral and alkaline hydrolysis reactions follow a pseudo-first order process, however it has been suggested that the presence of acid facilitates a catalytic rate of degradation after an initial incubation period.

Multiple studies have addressed the decomposition reactions of nitrate esters following the initial scission of the nitrate group [?, ?, ?, ?, ?, ?]

In this section, secondary and extended reaction schemes for the low temperature ageing of **NC!** are explored. Decomposition pathways defined by Camera *et al.* and Aellig *et al.* are probed to determine the reactions responsible for the experimentally observed degradation products. The reactions found to be energetically feasible from the proposed routes will be scrutinised to determine whether an autocatalytic pathway can be formed from the energetically validated reaction schemes.

4.2 Methodology

The reaction schemes proposed by Chin, Camera and Aellig *et al.* were applied to the degradation of **NC!** as the subsequent steps following denitration *via* homolytic fission, intramolecular elimination of HNO_2 or acid hydrolysis.

Scheme 4.2 - 4.4

The species reactions were geometry optimised using **wb97xd!** (**wb97xd!**), and **B3LYP!** (**B3LYP!**) functionals, in both vacuum and solvent. The reactions were modelled using ethyl nitrate as a test system before expansion to the full **C2** monomeric model. The **DG!** (**DG!**) were used to determine the feasibility of a reaction. Where the choice of method lead to a variation in the result

4.2.1 Computational details

All geometry optimisations were performed in **G09!** (**G09!**), using the **wb97xd!** and **B3LYP!** functionals. Optimisations were repeated with **PCM!** (**PCM!**) to introduce solvent effects.

4.3 Results and Discussion

4.3.1 Thermodynamics of Ethyl Nitrate reactions

The reaction energies for the proposed schemes

Collation of the above schemes to fit the starting products from denitration:

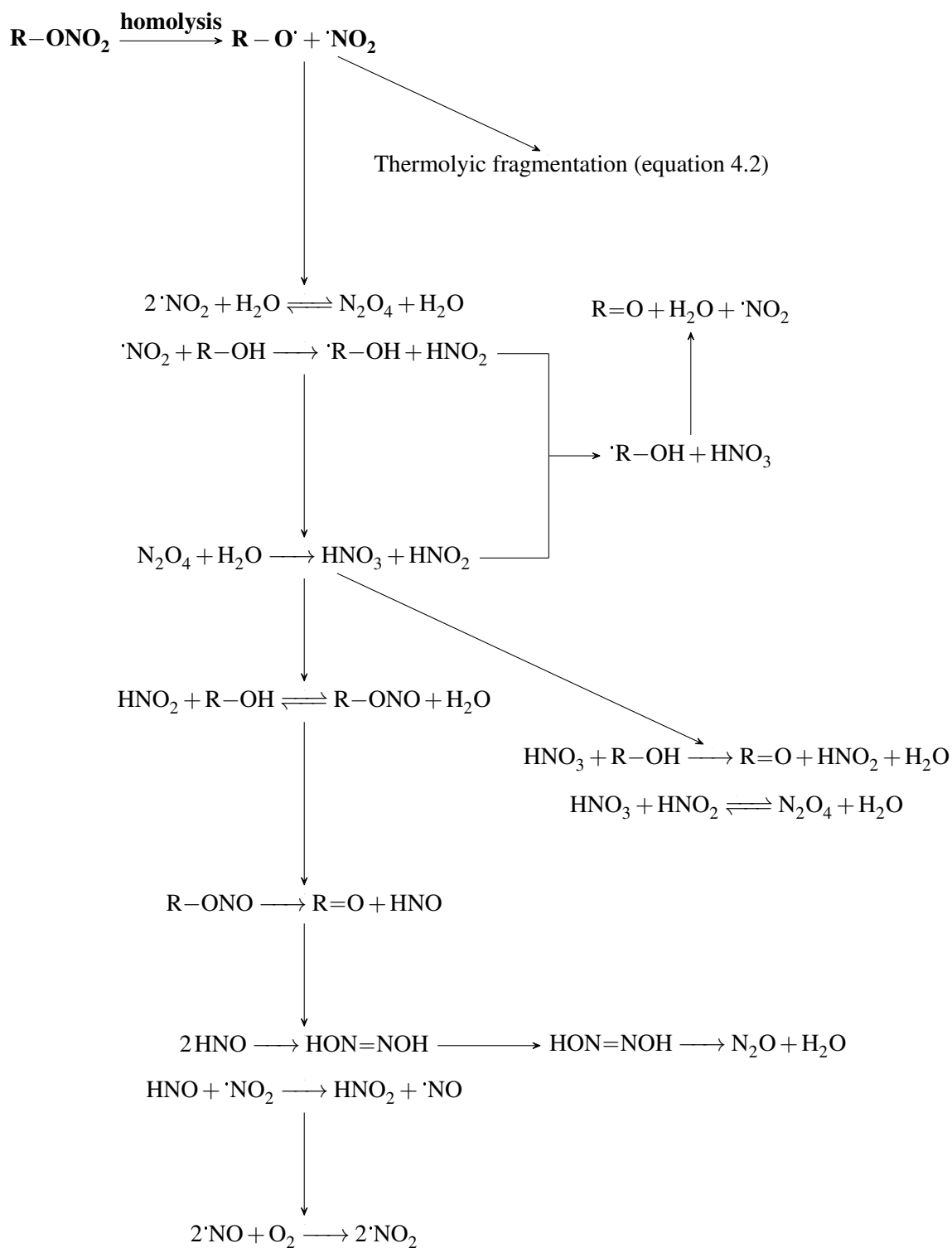
4.4 Summary

Table 4.1: Free energies of protonation for each oxygen site on ethyl nitrate.

Protonated site		ΔG_r /kcal mol ⁻¹			
		wb97xd!	PCM	B3LYP!	PCM
Terminal (up)	CH ₃ CH ₃ ONO ₂ H ⁺	0.0072	0.0083	0.0064	0.0077
Terminal (down)	CH ₃ CH ₃ ONO ₂ H ⁺	-0.0195	0.0140	-0.0219	0.0101
Bridging	CH ₃ CH ₃ O(H ⁺)NO ₂	-0.0195	0.0140	-0.0219	0.0101

Table 4.2: Energies of nitrate ester decomposition reactions proposed by Camera [?], Chin [?] and Aellig [?]. R = CH₃CH₂ for ethyl nitrate, and R = (H₃CO)₂C₆H₉O₃ (bi-methoxy capped glucopyraonse monomer unit).

Reaction	ΔG_r /kcal mol ⁻¹			
	wb97xd!	PCM	B3LYP!	PCM
NO ₂ ⁺ + 2H ₂ O \rightleftharpoons HNO ₃ + H ₃ O ⁺	-0.8965	-1.3388	1.7703	2.4646
2'NO + O ₂ \longrightarrow 2'NO ₂	-20.7705	-21.9731	-21.1604	-22.1590
2'NO ₂ \rightleftharpoons N ₂ O ₄	-0.1222	-1.3104	0.5418	0.1556
HNO ₃ + HNO ₂ \rightleftharpoons N ₂ O ₄ + H ₂ O	-2.2516	-1.8541	-5.1314	-4.1801
N ₂ O ₄ \rightleftharpoons 2'NO ₂	0.1235	1.4616	-0.5393	-0.1556
4HNO ₃ \rightleftharpoons 4NO ₂ + 2H ₂ O + O ₂	53.3503	58.3645	42.6094	46.9356
2'NO ₂ + H ₂ O \rightleftharpoons N ₂ O ₄ + H ₂ O	-0.1222	-1.4616	0.5393	0.1556
N ₂ O ₄ + H ₂ O \longrightarrow HNO ₃ + HNO ₂	2.2516	1.8541	5.1314	4.1801
'NO ₂ + HNO \longrightarrow HNO ₂ + 'NO	-28.2164	-28.6682	-27.3269	-27.6255
2'NO + O ₂ \longrightarrow 2'NO ₂	-59.8947	-60.4724	-60.4687	-60.9960
2HNO \longrightarrow HON=NOH	-38.9693	-39.7158	-36.6276	-37.4081
HON=NOH \longrightarrow N ₂ O + H ₂ O	-48.0829	-48.1843	-50.5531	-50.7490
Ethyl nitrate (R = CH ₃ CH ₂)				
R-OH + HNO ₃ \longrightarrow R=O + HNO ₂ + H ₂ O	-34.0622	-38.4275	-37.5940	-41.7703
R-OH + 'NO ₂ \longrightarrow 'R-OH + HNO ₂	16.3762	13.9230	15.8873	13.6994
'R-OH + HNO ₃ \longrightarrow R=O + H ₂ O + 'NO ₂	-50.4384	-52.3505	-53.4813	-55.4715
R-OH + HNO ₂ \rightleftharpoons R-ONO + H ₂ O	-3.2054	-3.2760	-2.6410	-2.9490
R-ONO \longrightarrow R=O + HNO	-1.4963	-5.8218	-4.3672	-8.5012
NC! monomer (R = (H ₃ CO) ₂ C ₆ H ₉ O ₃)				
R-ONO ₂ + H ₂ O \longrightarrow R-OH + HNO ₃	0.6754	5.6309	0.6124	-0.7012
R-OH + 'NO ₂ \longrightarrow 'R-OH + HNO ₂	14.7130	11.1516	13.0341	23.2098
'R-OH + HNO ₃ \longrightarrow R=O + H ₂ O + 'NO ₂	-51.4382	-49.4947	-54.7483	-56.3693
R-OH + HNO ₂ \rightleftharpoons R-ONO + H ₂ O	-4.4314	-7.3023	-4.3061	-0.1783
R-ONO \longrightarrow R=O + HNO	-2.9333	-1.7111	-6.8223	-11.2058



Scheme 4.2: Proposed degradation pathway starting from the homolysis products of a nitrate ester, derived from the schemes presented by Camera [?] and Aellig[?].

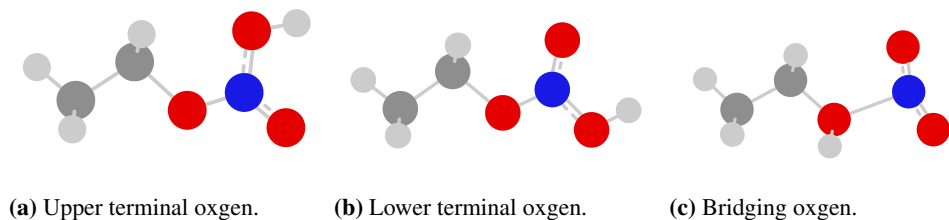
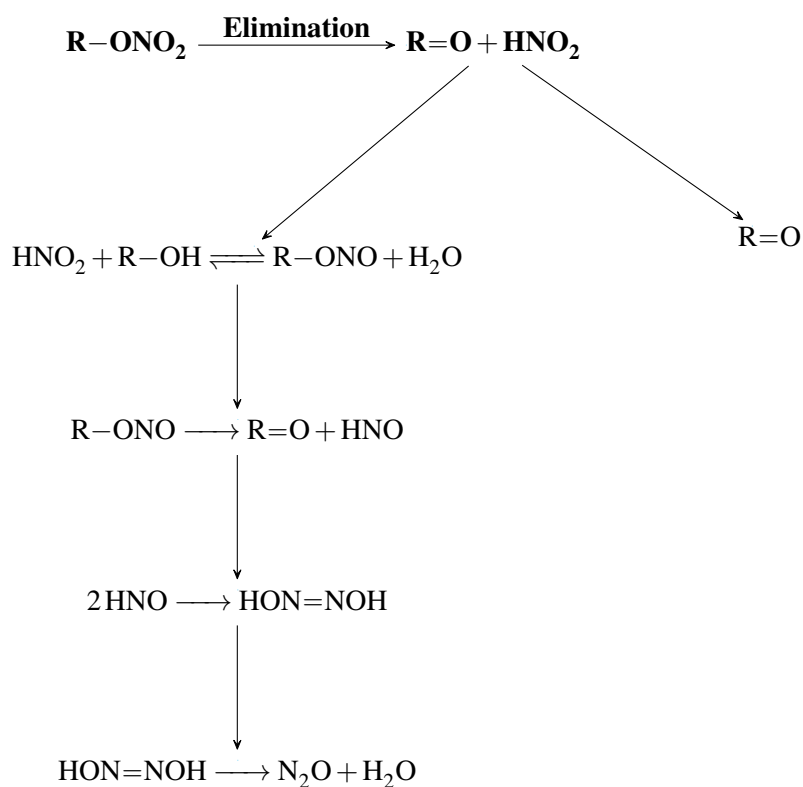
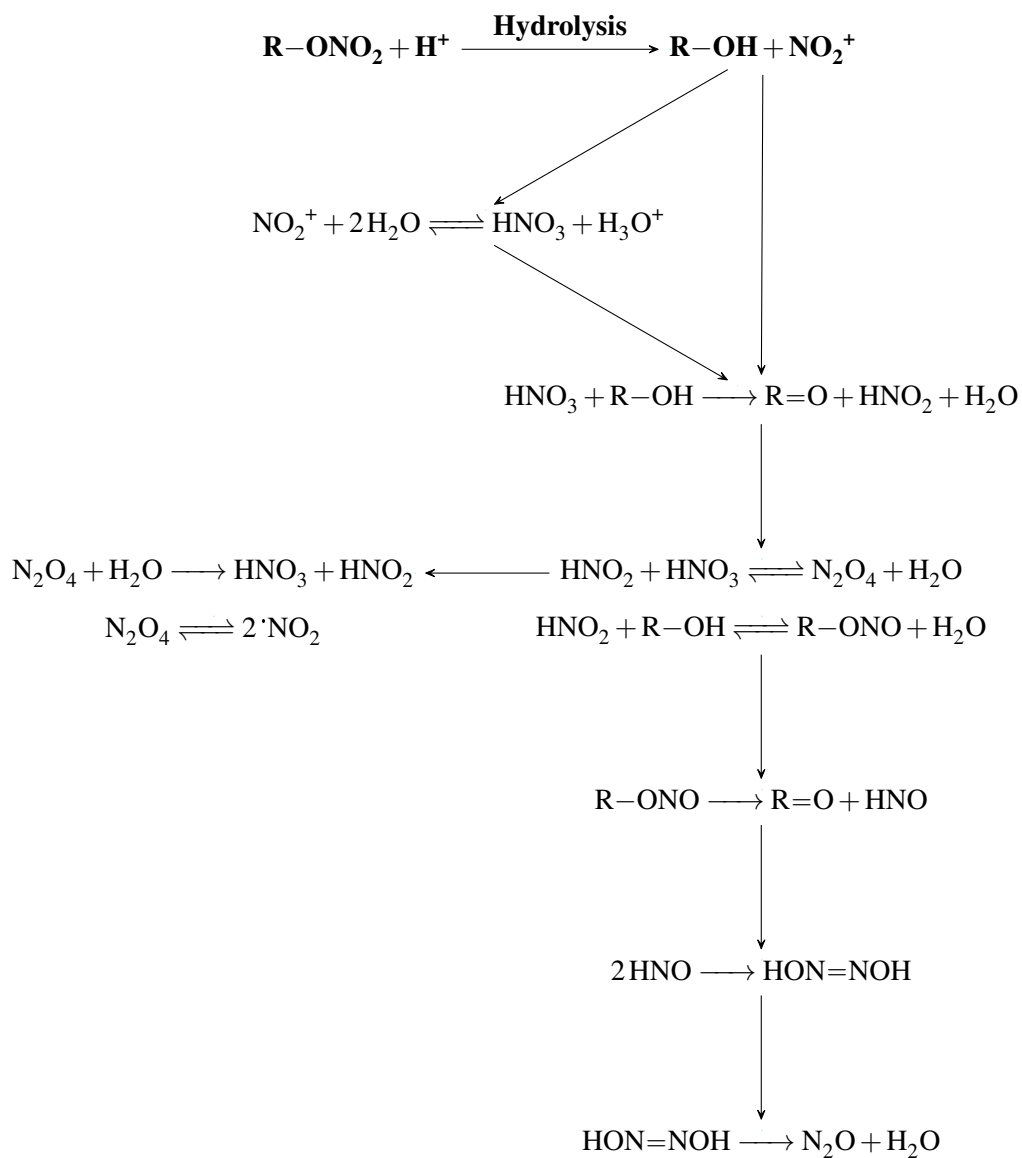


Figure 4.2: Possible sites of protonation on ethyl nitrate.



Scheme 4.3: Proposed degradation pathway starting from the elimination of HNO_2 from a nitrate ester, derived from the schemes presented by Camera [?] and Aellig[?].



Scheme 4.4: Proposed degradation pathway starting from the acid hydrolysis of a nitrate ester, derived from the schemes presented by Camera [?] and Aellig[?].

