Determining the dominant degradation mechanisms 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

The dominant degradation pathways of nitrocellulose (NC) were investigated, using quantum mechanics (QM) methods to probe the primary denitration routes, followed by key secondary reactions. The polymer structure was truncated in order to facilitate density functional theory (DFT) studies into the mechanistic details of denitration at individuate nitrate sites. Comparison of monomer, dimer and trimer units of the polymer using quantum theory of atoms in molecules (QTAIM) topology analysis of interaction sites, analysis of the electrostatic potential (ESP) and charges showed that the most suitable model for study of the decomposition reactions was β-glucopyranose monomer, bi-capped with methoxy groups. The model was nitrated at the C2 position, to mimic the most stable nitration site [1]. The primary thermolytic and hydrolytic denitration routes were explored using transition state (TS) searches and potential energy surface (PES) scans. It was found that the thermolytic behaviour of the NC denitration step matched the energy profile of other nitrate esters [2]. Protonation at the bridging oxygen site of the nitrate was found to be the most likely to lead to denitration. It was not possible to isolate a TS for the hydrolytic reaction, though a number of coordination schemes were tested. Secondary processes following initial denitration were examined. Ethyl nitrate was used as a test system before extension to the monomer. Different reaction pathways for decomposition, with forward propagation of the evolved species to the reaction step, revealed that $^{\bullet}NO_2$ was the most likely cause for the the experimentally observed autocatalytic rate of degradation.

Impact Statement

This study examines the degradation properties of NC, shedding light on the mechanistic details of decomposition that are yet currently either unknown, or are unclear with contradictory views in existing literature. NC is used in a massive variety of products, with utilisation in household, industrial, military and medicinal applications.

Improved understanding of the fundamental chemistry in the degradation of NC could benefit in the following key impact areas:

Knowledge & collective benefit

- Broaden understanding and depth of knowledge in the area of NC degradation, with the view to validate or reject conflicting schemes in literature.

- Improve conservation procedures for existing and legacy NC products, such as cinematographic film, artworks and historical munitions with better understanding of the handling procedures for these aged products.

Environmental

Design next generation NC products more environmentally friendly, in terms of durability and recycle-ability.

Improve and clean up industrial processes for more environmentally benign production process.

Design appropriate NC disposal methods, other than the existing harsh chemical or incineration treatment, with opportunity to feed back into other processes, such as the production of fertiliser.

Safety

Guidelines on safety and usage could be refined based on detailed knowledge of the degradation reactions, instead of current guidelines based on more crude, aggregate experimental

observations.

Industrial & Commercial

More adaptability in the production of NC and its formulation into products, in the case that the variety of source cellulose feedstock changes due to supply chain issues.

Streamline industrial processes to specific reactivity requirements, based on detailed mechanistic considerations, leading to cost saving.

Innovation

Create new products, not limited by previous assumptions about the shelf life and reactivity. Facilitate the design of products for applications that were previously not known that the material was suitable for.

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Abbreviations

%N	percentage nitrogen by mass
2-NDPA	2-Nitrodiphenylamine
AIMD	*ab initio* 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
CH$_3$CH$_3$	NC repeat unit with two $-OCH_3$ capping groups
CH$_3$OH	NC repeat unit with $-OCH_3$ capping group on ring 1 and $-OH$ group on ring 2
CCP	cage critical point
CP	critical point
DFT	density functional theory
DFT-D	density functional theory with dispersion correction
DSC	differential scanning calorimetry
DOS	degree of substitution
DPA	diphenylamine

EM	energetic materials
EN	ethyl nitrate
ESP	electrostatic potential
G09	Gaussian 09 revision D.01
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

NCP	nuclear critical point
NG	nitroglycerine
NMR	nuclear magnetic resonance spectroscopy
OHCH$_3$	NC repeat unit with $-$OH capping group on ring 1 and $-$OCH$_3$ group on ring 2
PCM	polarisable continuum model
PES	potential energy surface
PETN	pentaerythritol tetranitrate
PETRIN	pentaerythritol trinitrate
QM	quantum mechanics
QTAIM	quantum theory of atoms in molecules
RCP	ring critical point
RESP	restrained electrostatic potential atomic partial charges
RHF	restricted HF
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$_N$2	bi-molecular nucleophilic substitution reaction
STO	Slater type orbitals
TG	thermogravitmetric analysis

TS	transition state
UFF	universal force field
UV	ultraviolet
UVvis	ultraviolet–visible spectroscopy
vdW	van der Waals
ωB97X-D	ωB97X-D long-range corrected hybrid functional
ZPE	zero-point energy

Bibliography

[1] Manoj K Shukla and Frances Hill. Computational elucidation of mechanisms of al-kaline hydrolysis of nitrocellulose: dimer and trimer models with comparison to the corresponding monomer. *The journal of physical chemistry. A*, 116(29):7746–55, 2012.

[2] Roman V. Tsyshevsky, Onise Sharia, and Maija M. Kuklja. Thermal Decomposition Mechanisms of Nitroesters: Ab Initio Modeling of Pentaerythritol Tetranitrate. *The Journal of Physical Chemistry C*, 117(35):18144–18153, sep 2013.