Computational Study of the Ageing Processes in Nitrocellulose

Amy J. Lai

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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 $^{\cdot}NO_2$ was the most likely cause for the the experimentally observed autocatalytic rate of degradation.

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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_3CH_3	NC repeat unit with two $-OCH_3$ capping groups
CH_3OH	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_N2 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 alkaline 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.