Impact Statement

This study examines the degradation properties of nitrocellulose (NC), shedding light on the mechanistic details of decomposition that are yet currently either unknown, or are unclear in existing literature. NC is used in an extensive 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 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 deconflict competing schemes in literature.
- Improve conservation practices for existing and legacy NC products of cultural value, such as cinematographic film, artworks and historical munitions with better information on environmental conditions most impacting the decomposition pathways.

Environmental

- Inform improved NC disposal methods, avoiding existing harsh chemical and incineration treatments, with opportunity to feed back into other manufacture streams such as the production of fertiliser.
- Facilitate the design of next generation NC products with lower environmental impact, in terms of durability and recycle-ability, with cleaner industrial processes.

Safety

- Refine guidelines on safety and usage, based on detailed knowledge of the degradation mechanisms, improving upon current practices based on aggregate experimental observations.

Industrial & commercial

- Improve versatility and adaptability in NC production and its product formulations, in view of varying cellulose feedstock sources due to supply chain fluctuation.
- Streamline industrial processes to specific reactivity requirements, based on detailed mechanistic considerations regarding shelf life and interaction with other components, leading to cost saving and better performance of final product.

Innovation

- Allow the design of new NC products, not limited by crude understanding about the material shelf life and reactivity, leading to novel applications.

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