Nitrooxides in Mechanistic Studies: Ageing of Gold Nanoparticles and Nitroxide Transformation in Acids

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Abstract

The work described in this thesis includes the applications of nitroxide in the mechanistic studies of two very different research topics.

Chapter 2 describes the investigation of ageing of gold nanoparticles (AuNPs) and its mechanistic implications. By utilizing a customized bisnitroxide disulfide, ligand place-exchange reactions of AuNPs were studied by Electron Paramagnetic Resonance (EPR) Spectroscopy and a nitroxide spin label was introduced onto the gold surface in the process. Ageing of thiolate protected AuNPs results in reduced reactivity in the disulfide exchange. By studying the ligand and temperature dependence of this process and the effect of ageing on the maximum extent of exchange, the presence of different binding sites on the surface of AuNPs was proposed.

Chapter 3 describes the mechanistic studies of nitroxide-based polymerization inhibitors in various organic monomers. The presence of nitroxide radicals was utilized to report dissolved oxygen concentration which is essential in the inhibition of polymerization. Oxygen-related broadening was deconvoluted from the EPR spectra of nitroxide radicals using an oximetry fitting method. By adopting this method, the inhibition mechanism and associated chemistry of nitroxides in self-initiated polymerization of acrylic acid was investigated. The synergism of nitroxides with other types of inhibitors was proposed. An unusual decay of nitroxide radicals in acid at high temperature was observed.

Following Chapter 3, Chapter 4 describes the detailed mechanistic investigation of nitroxide decay in acid at high temperature. N-oxoammonium salt, a product of acid-catalyzed disproportionation of nitroxides, was found to decompose at high temperature. Mechanistic investigation of this reaction leads to identification of the important role of hydroxylamine in the mechanism of nitroxide inhibited polymerization of acidic monomers.
Declaration

This thesis is a summary of the research work carried out in the Department of Chemistry, University of York, between October 2006 and September 2010. It has not, either in part or as a whole, been submitted for a degree or diploma or other qualification at any other University.

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List of Abbreviations

Abs – absorbance
aq – aqueous solution
a.u. – arbitrary units
AuNPs – gold nanoparticles
DIS3 –

\[
\begin{align*}
\text{S} & \text{NH} & \text{N} & \text{O} \\
\text{S} & \text{H} & \text{N} & \text{O}
\end{align*}
\]

EI – electron impact ionization
EPR – Electron Paramagnetic Resonance
ESI – electrospray ionization
EXP – experimental
FID – flame ionization detector
g – gram(s)
GC – Gas Chromatography
gem – germinal
GPC – Gel Permeation Chromatography
HR – high resolution
hrs – hour(s)
4HT – 4-hydroxy-TEMPO
IR – infrared
M – molar
MEHQ – monomethyl ether of hydroquinone (4-Methoxyphenol)
Me – methyl, CH₃
mg – milligram(s)
Mhz – megahertz
min – minute(s)
ml – millilitre(s)
µl – microlitre
MS – Mass Spectrometry
m/z – charge to mass ratio
n – normal
Na-ASC – sodium L-ascorbate
nm – nanometre(s)
NMR – Nuclear Magnetic Resonance
ns – nanosecond(s)
4OT – 4-oxo-TEMPO
p – para-
PhNHNH₂ – phenylhydrazine
PPh₃ – triphenylphosphine
ppm – part(s) per million
ppt – part(s) per trillion
PTZ – phenothiazine
R.T. – room temperature
s – second(s)
SOMO – singly occupied molecular orbital
TEM – Transmission Electron Microscopy
TEMPO(T) – 2,2,6,6-tetramethyl-1-piperidinyloxyl
TEMPOH(TOH) – TEMPO hydroxylamine
TGA – Thermogravimetric
TH⁺ – protonated TEMPO
TLC – Thin Layer Chromatography
T=O⁺ – oxoammonium salt from TEMPO
TOAB – tetraoctylammonium bromide
TOH₂⁺ – protonated TEMPOH
UV-vis – Ultraviolet-visible
v/v – volume to volume ratio
w/w – weight to weight ratio
# Table of Contents

## CHAPTER 1 INTRODUCTION

1.1. ‘YOU CANNOT CONNECT THE DOTS LOOKING FORWARDS, YOU CAN ONLY CONNECT THEM LOOKING BACKWARDS.’ ........................................... 1

1.2. ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY .......... 2

1.2.1. BASIC PRINCIPLES OF ELECTRON PARAMAGNETIC RESONANCE ......................................................... 2
1.2.2. DETECTION OF RESONANCE ................................................................. 4
1.2.3. EPR INSTRUMENTATION ...................................................................... 5
   1.2.3.1. Microwave bridge ........................................................................ 6
   1.2.3.2. Magnetic field modulation ........................................................... 7
   1.2.3.3. Variable temperature measurements ........................................... 7
1.2.4. EPR SPECTRAL PARAMETERS .......................................................... 8
   1.2.4.1. g-factor ....................................................................................... 8
   1.2.4.2. Hyperfine interaction ................................................................. 9
   1.2.4.3. Spectral linewidth and intensity .................................................. 13
   1.2.4.4. Intensity of EPR spectra ............................................................. 18
   1.2.4.5. Dynamics and diffusion ............................................................. 18
1.2.5. BIRADICALS .............................................................................. 20
1.2.6. APPLICATIONS OF CW-EPR SPECTROSCOPY ......................... 22
   1.2.6.1. Direct detection ....................................................................... 22
   1.2.6.2. Spin labelling ........................................................................... 22

## CHAPTER 2 REDUCED REACTIVITY OF AGED GOLD NANOPIRATES

2.1. INTRODUCTION .................................................................................. 27

2.1.1. GOLD NANOPIRATES .................................................................... 27
2.1.2. APPLICATIONS OF AUNPs ............................................................ 28
   2.1.2.1. Catalysis ................................................................................... 28
   2.1.2.2. Bio-medical applications ......................................................... 28
2.1.3. SYNTHESIS OF AUNPs ................................................................. 29
   2.1.3.1. Citrate reduction method .......................................................... 29
   2.1.3.2. Brust-Schiffrin method ............................................................. 30
   2.1.3.3. AuNPs protected by phosphane .............................................. 31
2.1.4. PARTICLE SIZE CONTROL ........................................................... 32
   2.1.4.1. Size control by adjusting synthetic conditions ......................... 32
   2.1.4.2. Post-synthesis modification ...................................................... 33
   2.1.4.3. Structure and morphology of AuNPs ......................................... 34
   2.1.4.4. Functionalization of AuNPs ...................................................... 35
   2.1.4.5. Mechanism of ligand exchange reaction .................................. 36
   2.1.4.6. Packing, migration and dynamics of the ligands on AuNPs ...... 40
   2.1.4.7. Ageing of AuNPs ................................................................... 41
2.1.5. AIM AND OBJECTIVES ................................................................. 42

2.2. INVESTIGATION METHODOLOGY ..................................................... 42

2.2.1. TARGET AUNPs ......................................................................... 42
2.2.2. ANALYTICAL METHOD SURVEY .................................................. 43
2.2.3. MODEL SYSTEM ......................................................................... 44

2.3. GENERAL SYNTHESIS AND CHARACTERIZATION OF AUNPs ....... 45
CHAPTER 3 MECHANISTIC STUDY OF NITROXIDE-BASED POLYMERIZATION INHIBITORS

3.1. INTRODUCTION ........................................................................................................ 77

3.1.1. NITROXIDE RADICALS ......................................................................................... 77
   3.1.1.1. Synthesis of nitroxide radicals ........................................................................ 78
   3.1.1.2. General chemistry of nitroxide radicals .......................................................... 79
   3.1.1.3. Applications of TEMPO derivatives ................................................................. 86
3.1.2. FREE RADICAL POLYMERIZATION AND INHIBITION ........................................ 89
   3.1.2.1. Initiation, propagation and termination steps ................................................... 90
   3.1.2.2. Self-initiation mechanism .............................................................................. 91
   3.1.2.3. Inhibition and retardation mechanism ............................................................ 94
3.1.3. AIMS AND OBJECTIVES ...................................................................................... 99

3.2. METHODOLOGY DEVELOPMENT FOR MONITORING NITROXIDE INHIBITED POLYMERIZATION ........................................................................ 100

3.2.1. MONITORING O₂ CONCENTRATION .................................................................... 100
   3.2.1.1. Analytical method survey ............................................................................ 100
   3.2.1.2. EPR oximetry ............................................................................................... 101
3.2.2. METHODOLOGY DEVELOPMENT FOR EPR OXIMETRY ....................................... 102
   3.2.2.1. Fitting method ............................................................................................. 102
   3.2.2.2. EPR oximetry via convolution-based fitting method ..................................... 103
3.2.3. OXIMETRY FITTING METHOD IN NITROXIDE INHIBITED METHYL METHACRYLATE AND ACRYLONITRILE ...................................................................................... 105
   3.2.3.1. 4HT inhibited spontaneous polymerization of methyl methacrylate and acrylonitrile .................................................................................................................. 106
3.2.4. METHODOLOGY LIMITATIONS .......................................................................... 108

4.1. Typical Synthesis Protocol .................................................................................... 45
4.2. Characterization of AUNPs .................................................................................. 45

4.2.1. REACTION ORDER ............................................................................................. 46
   4.2.1.1. General data collection and treatment procedure .......................................... 47
   4.2.1.2. Ligand exchange of C₆S-AuNPs: reaction order .......................................... 48
   4.2.1.3. Ligand exchange of C₈S- and C₁₀S-AuNPs: reaction order ......................... 50
4.2.2. REDUCED REACTIVITY OF AGED AUNPS IN LIGAND EXCHANGE REACTIONS ...... 52
   4.2.2.1. Ageing effect on C₆S-AuNPs ......................................................................... 52
   4.2.2.2. Effect of reaction temperature on ageing effect ............................................. 53
   4.2.2.3. Outgoing ligand dependence of ageing effect .............................................. 56
4.2.3. AGEING AND CONCURRENT SIZE VARIATION OF AUNPS ................................. 58
4.2.4. REDUCED REACTIVITY OF AGED AUNPS IN CYANIDE INDUCED DECOMPOSITION ... 60
   4.2.4.1. General data collection and treatment procedure ........................................ 60
   4.2.4.2. Ligand exchange of C₆S-AuNPs ................................................................. 61
   4.2.4.3. Reaction order ............................................................................................. 61
   4.2.4.4. Effect of reaction temperature on ageing effect ......................................... 62
   4.2.4.5. Outgoing ligand dependence of ageing effect ............................................. 62
4.2.5. CONCLUSIONS ON AGEING EFFECT OF AUNPs ............................................. 62

5.5. EXTENT OF LIGAND EXCHANGE REACTIONS OF AUNPS WITH DISULFIDES ................................................ 64

5.5.1. DOES MAXIMUM EXTENT OF LIGAND EXCHANGE REACTION CHANGE WITH AGEING? ................................................................. 64
5.5.2. AUNP/DISULFIDE RATIO DEPENDENCE ON THE MAXIMUM EXTENT OF LIGAND EXCHANGE REACTIONS ................................................................. 66
5.5.3. THE EXTENT OF LIGAND EXCHANGE REACTION AT DIFFERENT TEMPERATURE ...... 67
5.5.4. CONCLUSIONS ON EXTENT OF LIGAND EXCHANGE ....................................... 68

5.6. CONCLUSIONS .......................................................................................................... 70
3.3. INVESTIGATION OF SPONTANEOUS POLYMERIZATION OF ACRYLIC ACID INHIBITED BY NITROXIDE RADICALS .......................... 109
3.3.1. INTRODUCTION ........................................................................................................... 109
3.3.2. INVESTIGATION OF SYNERGISTIC INHIBITION OF SELF-INITIATED ACRYLIC ACID POLYMERIZATION ........................................ 110
   3.3.2.1. Inhibition of self-polymerization of acrylic acid by 4HT/MEHQ and 4HT/PTZ mixtures ............................................................................. 110
   3.3.2.2. The effect of hydroxylamine on the inhibition mechanism of 4HT in self-polymerization of acrylic acid ........................................ 110
3.3.3. MECHANISTIC STUDY ON 4HT IN SELF-POLYMERIZATION OF ACRYLIC ACID ....... 117
3.3.4. CONCLUSIONS ON MECHANISTIC INVESTIGATION OF INHIBITED SPONTANEOUS POLYMERIZATION OF ACRYLIC ACID .................. 120

3.4. KINETIC AND MECHANISTIC INVESTIGATIONS OF ACID-CATALYZED TEMPO DISPROPORTIONATION ........................................ 121
3.4.1. INTRODUCTION ........................................................................................................... 121
3.4.2. KINETIC STUDY OF ACID-CATALYZED TEMPO DISPROPORTIONATION ............. 121
   3.4.2.1. The role of substituent in the 4-position .................................................................. 122
   3.4.2.2. TEMPO disproportionation in acrylic acid .......................................................... 123
   3.4.2.3. Nitrooxide radical disproportionation in acetic and propionic acid ................. 125
   3.4.2.4. TEMPO disproportionation in sulphuric acid ....................................................... 126
3.4.3. TEMPERATURE DEPENDENT KINETIC MODEL OF TEMPO DISPROPORTIONATION . 130
   3.4.3.1. Kinetic model of TEMPO disproportionation reaction ..................................... 130
   3.4.3.2. Fitting experimental data to the kinetic model ...................................................... 133
3.4.4. COMPROPORTIONATION OF TEMPOH AND N-OXOAMMONIUM SALT ............ 134
3.4.5. CONCLUSIONS OF ACID-CATALYZED TEMPO DISPROPORTIONATION ................ 136

3.5. CONCLUSIONS .................................................................................................................. 137

CHAPTER 4 TEMPO DECAY IN ACID AT HIGH TEMPERATURE

4.1. INTRODUCTION .............................................................................................................. 144
4.2. AIMS AND OBJECTIVES ............................................................................................... 146
4.3. THERMAL DECOMPOSITION OF TEMPO IN ACID: DECOMPOSITION OF N-OXOAMMONIUM SALT ........................................ 146
   4.3.1. IRREVERSIBLE TEMPO DECAY IN ACID AT HIGH TEMPERATURE ............... 146
   4.3.2. THERMAL DECOMPOSITION OF N-OXOAMMONIUM SALT .......................... 148
      4.3.2.1. The effect of acidity on thermal decomposition of oxoammonium salt ........... 149
      4.3.2.2. The effect of O₂ on thermal decomposition of oxoammonium salt ............... 151
      4.3.2.3. Light dependence of thermal decomposition of oxoammonium salt .......... 151
      4.3.2.4. Kinetic model for thermal decomposition of oxoammonium salt ............... 152
   4.3.3. THERMAL DECOMPOSITION OF TEMPO IN H₂O ......... ................................. 153
   4.3.4. FORMATION OF A UV-ACTIVE COMPOUND IN THERMAL DECOMPOSITION OF OXOAMMONIUM SALT ............................................. 155

4.4. PRODUCT ANALYSIS OF THERMAL DECOMPOSITION OF OXOAMMONIUM SALT ................................................................. 156
   4.4.1. IDENTIFICATION OF THE MAJOR REACTION PRODUCT ................................. 156
      4.4.1.1. Fast electron transfer between TEMPO and oxoammonium cation .......... 156
      4.4.1.2. Identification of hydroxylamine as the major reaction product of thermal decomposition of oxoammonium salt ......................... 158
   4.4.2. QUANTIFICATION OF THE YIELD OF HYDROXYLAMINE ............................... 161
4.5. THE MECHANISM OXOAMMONIUM SALT DECOMPOSITION ..........165
  4.5.1. HYDROLYSIS MECHANISM .................................................. 165
  4.5.2. RING OPENING MECHANISM ................................................. 166
  4.5.2.1. Detection of possible ring opening product by EPR spectroscopy ……… 166
  4.5.2.2. Detection of NO₃⁻ in the reaction product ................................ 167
  4.5.2.3. Ring-opening decomposition of 4-oxo-TEMPO .......................... 168

4.6. OXOAMMONIUM SALT DECOMPOSITION CARRIED OUT ON A LARGE
    SCALE .......................................................................................... 170
  4.6.1. AQUEOUS PHASE .................................................................. 171
  4.6.1.1. Analysis of the aqueous phase product by NMR spectroscopy ....... 171
  4.6.1.2. Titration of the aqueous phase product .................................. 172
  4.6.2. ANALYSIS OF ORGANIC PHASE ............................................ 176
  4.6.2.1. UV-vis analysis .................................................................. 176
  4.6.2.2. TLC ................................................................................. 177
  4.6.2.3. GC-MS ............................................................................ 177
  4.6.2.4. MS: ESI ........................................................................... 186
  4.6.2.5. NMR spectroscopy ............................................................. 190
  4.6.3. ANALYSIS OF GAS PHASE PRODUCT ................................... 191
  4.6.3.1. Analysis by GC-FID .......................................................... 192
  4.6.3.2. Analysis by gas phase IR ..................................................... 192

4.7. CONCLUSIONS ............................................................................. 195
  4.7.1. MECHANISM OF THERMAL DECOMPOSITION OF OXOAMMONIUM
         SALT ....................................................................................... 196
  4.7.2. YIELD CALCULATIONS AND MASS BALANCE .......................... 198
  4.7.3. MECHANISM OF TEMPO DECAY IN ACID AT HIGH TEMPERATURE 199
  4.7.4. PERSPECTIVES AND FUTURE WORK ................................. 200

CHAPTER 5 EXPERIMENTAL

5.1. CHEMICALS AND ANALYSIS TECHNIQUES .................................. 203

5.2. GENERAL PROCEDURES OF EPR EXPERIMENTS .......................... 206
  5.2.1. PREPARING EPR SAMPLES .................................................. 206
  5.2.2. DEGASSING EPR SAMPLES .................................................. 207
  5.2.3. EPR KINETICS .................................................................... 207

5.3. DATA PROCESSING PROCEDURES ............................................. 208
  5.3.1. KINETIC STUDIES ................................................................. 208
  5.3.2. OXIMETRY FITTING .............................................................. 208

5.4. SYNTHESIS ................................................................................. 209