Chemical trapping of nitric oxide by aromatic nitroso sulfonates

A Thesis submitted for the Degree of

DOCTOR OF PHILOSOPHY

By

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STATEMENT OF ORIGINALITY

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text. I give consent to this copy of my thesis, when deposited in the University library, being made available for loan and photocopying subject to the provision of the Copyright Act 1968.

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Date: 28 March 2013
STATEMENT OF AUTHORSHIP

I hereby certify that the work embodied in this thesis contains published papers of which I am a joint author. I have included as part of the thesis a written statement, endorsed by my supervisors, attesting to my significant contribution to the joint publications.

____________________________  Date: 28 March 2013

Wendy Venpin
STATEMENT OF CONTRIBUTION OF OTHERS

We, the undersigned, attest that Research Higher Degree candidate, Wendy Koo Pao Foon Venpin, has devised the experimental program, conducted experiments, analysed data, performed computational chemistry calculations and has written all papers included in this thesis. Professors Bogdan Z. Dlugogorski, Eric M. Kennedy and John C. Mackie provided advice on the experimental program, project direction and assisted with the editing of the papers, consistent with normal supervisors-candidate relations.

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Professor Bogdan Z. Dlugogorski Date:

______________________________
Professor Eric M. Kennedy Date:

______________________________
Professor John C. Mackie Date:
DEDICATIONS

To my late father, Charles Venpin, who provided an example of a hardworker and inspired my love for science and engineering.
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This thesis investigates the employment of spin traps as NOx scavengers to control noxious NOx formation during nitrosation reactions. Most notably, the reaction conditions studied are relevant to the sensitisation of emulsion explosives activated by the chemical gassing, where the formation of these gases can trigger serious respiratory problems to explosives users. Spin traps are widely used by biochemists to detect and measure free radicals such as nitric oxide (NO) in biological systems. The spin trapping reaction involves the addition of a radical to the spin trap, which results in the formation of a complex adduct, detectable by electron paramagnetic resonance (EPR). Intuitively, as a result of the effect of the spin trapping reaction on free radical, these spin traps can potentially play an important role in the development of a new technology to reduce NOx emission.

Four aromatic ortho substituted nitroso compounds, 3,5-dibromo-4-nitrosobenzene sulfonate (DBNBS), nitrosobenzene sulfonate (NBS), 3,5-dimethyl-4-nitrosobenzene sulfonate (DMNBS) and 3,5-dichloro-4-nitrosobenzene sulfonate (DCNBS) were subjected to detailed experimental and theoretical investigation in this thesis. These compounds were synthesised by the oxidation of their corresponding amine compounds and characterised by infrared (IR), ultraviolet visible (UV-Vis), nuclear magnetic resonance (NMR) spectroscopy and nanostructured assisted laser desorption ionisation mass spectrometric (NALDI-MS).

The thesis initially studied the reaction of DBNBS with NO, where NO was generated in an acidic nitrite solution, conditions which are similar to the chemical gassing process of emulsion explosives, by examining gaseous and liquid products from the
reaction. Membrane inlet mass spectrometer (MIMS) analysis disclosed the presence of significant amount of nitrogen gas (N₂) in the gas phase, whereas ion chromatographic analysis of the reaction mixture disclosed elevated amounts of nitrate were formed during the gassing reaction.

During the reaction, DBNBS initially reacts with NO to form a short live DBNBS-NO adduct. The release of N₂ is a consequence of the homolytic cleavage of the C-N bond of a diazenyl radical. This assertion is based on quantum chemical calculations (Density Functional Theory) which validates the favourable formation of a diazenyl radical as well as oxygen. The elevated concentration of nitrate in solution provides additional evidence of the presence of oxygen released as a result of the decomposition of the radical intermediate (DBNBS-NO adduct). NALDI-MS analysis of liquid products in the study enabled the identification of 3,4,5-trinitrobenzene sulfonate (MW of 291.888 a.m.u) as the primary product from the reaction, and a number of other nitro compounds were also identified. Analysis of the gaseous and liquid products, in particular the NALDI-MS technique, demonstrates that the presence of nitrite leads to the formation of a competing reaction pathway whereby nitro group is introduced in the aromatic system through the coupling of nitrite with a phenyl radical.

A novel membrane NOx analyser and a stopped-flow UV-Vis spectrometer were employed to determine the rate of trapping of NO by DBNBS based on the proposed mechanism. The thermodynamic and kinetic properties of the dissociation of DBNBS dimer to its monomer, were first investigated as this step controls the trapping of NO by DBNBS. An equilibrium constant, $K_C$ of $(1.29 \pm 0.03) \times 10^{-3}$ (at 25 °C) for DBNBS dimer/monomer interchange was estimated, which indicates that, at equilibrium around 20 % of the dissolved DBNBS is present as monomer at room temperature, and
available for trapping NO under these conditions. The study of the reaction at temperatures ranging from 25 to 60 °C shows increasing monomer equilibrium concentrations as temperature rises.

Analysis of the measurements from the ex situ trapping of NO (where nitric oxide was generated via the rapid nitrosation of ascorbic acid) to a multistep reaction mechanism resulted in an estimate of the rate constant $k_{\text{Trap}}$ of 165 mol$^{-1}$ dm$^3$ s$^{-1}$. In contrast, the net rate of trapping was considerably lower with a value of 4.7 mol$^{-1}$ dm$^3$ s$^{-1}$ for the in situ reaction of DBNBS with NO, where NO is formed via the slow decomposition of nitrous acid.

The physicochemical properties of the four selected aromatic ortho substituted nitroso compounds were also examined. Since the four nitroso compounds exist in a monomer-dimer equilibrium with only the monomeric form behaving as a free radical scavenger, thermodynamic analysis of the dimer-monomer equilibrium was undertaken using UV-Vis spectrophometer.

The reactivity of the aromatic ortho substituted nitroso compounds towards NO was investigated, to determine the effect of substituents on the aromatic ring towards trapping efficiency in an aqueous system. The production of nitrogen gas and an elevated quantities of nitrate were observed during the reactions of nitroso compounds with NO suggesting that the homolytic cleavage of aryl radicals generally occurs when nitroso compounds reacts with NO as proposed previously for DBNBS.

The capacity of the aromatic nitroso sulfonates was investigated at ammonium nitrate (AN) concentration ranging from 0 to 7.5 mol dm$^{-3}$ for trapping NO. The solubility of DCNBS in AN solutions was the most affected among the four compounds and was
reflected by a notable decrease in the efficiency of NO removal by the compound with increasing AN concentrations.

Experiments in AN explosive established that chemical trapping of NO was more efficient when the nitroso compounds were added at the time of chemical gassing, rather than being part of the discrete phase of the emulsion. All nitroso compounds demonstrated an inhibitory effect on the amount of NO released from the chemical gassing of the emulsion explosive. Owing to the reduced efficiency in NO removal in AN solutions and AN emulsion, aromatic nitroso sulfonates are good NO scavengers with removal efficiency in NO of up to 70 % that can be achieved in sensitised AN emulsion.
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<td>AN</td>
<td>Ammonium nitrate</td>
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<tr>
<td>DBNBS</td>
<td>3,5-dibromo-4-nitrosobenzene sulfonate sodium salt</td>
</tr>
<tr>
<td>DCNBS</td>
<td>3,5-dichloro-4-nitrosobenzene sulfonate sodium salt</td>
</tr>
<tr>
<td>DETC</td>
<td>Diethyldithiocarbamate</td>
</tr>
<tr>
<td>DMNBS</td>
<td>3,5-dimethyl-4-nitrosobenzene sulfonate sodium salt</td>
</tr>
<tr>
<td>EDRF</td>
<td>Endothelium-derived relaxing factor</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
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<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>NO</td>
<td>Nitric oxide</td>
</tr>
</tbody>
</table>
NO$_2$  Nitrogen dioxide
N$_2$O  Nitrous oxide
NO$_2^-$  Nitrite
NO$_3^-$  Nitrate
NOCT  Nitric oxide cheletropic trap
PIBSA  polyisobutylene succinic anhydride
PTIO  2-phenyl-4,4,5,5-tetramethylimidazoline-1-yloxy-3-oxide
O$_2$  Oxygen
O$_2^-$  Superoxide
ONOO-  Peroxynitrite
SCR  Selective catalytic reduction
SNCR  Selective non-catalytic reduction
TLV-TWA  Threshold exposure limit time weighted average
UV-Vis  Ultraviolet visible