Nitric oxide formation in nitrosation reactions, with applications in the sensitisation of emulsion explosives

Submitted for the Degree of

DOCTOR OF PHILOSOPHY

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June, 2012

STATEMENT OF ORIGINALITY

The 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 provisions of the Copyright Act 1968.

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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 supervisor, attesting to my contribution to the joint publications.

Date:

Mark Rayson

STATEMENT OF CONTRIBUTION OF OTHERS

We, the undersigned, attest that the Research Higher Degree candidate, Mark Rayson, has devised the experimental program, conducted experiments, analysed data, performed computational chemistry calculations and has written all papers included in this thesis. Professors Bogdan Dlugogorski, Eric Kennedy and John Mackie provided advice on the experimental program, project direction and assisted with editing the papers, consistent with normal supervisor-candidate relations.

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ACKNOWLEDGEMENTS

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ABSTRACT

This thesis examines the rates and mechanisms of chemical reactions leading to production of nitrogen oxides during nitrosation reactions and, in particular, those occurring under conditions relevant to the sensitisation of emulsion explosives, where these toxic gases pose a hazard to explosive users. The decomposition of nitrous acid and nitrosyl thiocyanate were identified in the literature review as likely sources of nitrogen oxides during nitrosation reactions and were subjected to detailed experimental and computational studies.

Stopped-flow spectrophotometry was employed to study the decomposition of nitrous acid in order to resolve discrepancies in the rate constants reported in the literature. The decomposition reactions were examined under conditions where the rate limiting step comprised the hydrolysis of nitrogen dioxide (NO_2), enabling the derivation of a simplified rate law based on the known elementary reaction mechanism. The rate constant, 1.34×10^{-6} $M^{-1}s^{-1}$, is thought to be of higher accuracy than those in the literature as it does not depend on the rate of parallel reaction pathways or on the rate of interphase mass transfer of gaseous reaction products. The activation energy for the simplified rate law was established to be 107 kJ mol^{-1}. Quantum chemistry calculations indicate that the majority of the large activation energy results from the endothermic nature of the equilibrium $2HNO_2 \leftrightarrows NO + NO_2 + H_2O$. The rate constant for the reaction between nitrate ions and nitrous acid, which inhibits HNO_2 decomposition, was also determined.

The decomposition of nitrosyl thiocyanate (ONSCN) comprises a complex sequence of reaction steps involving three reaction pathways, and results in the formation of NO and $(SCN)_2$, with the latter undergoing a series of disproportion and hydrolysis reactions to ultimately yield SO_4^{2-}, HCN and SCN^-. The first reaction pathway involves an irreversible reaction second order in ONSCN, producing NO and $(SCN)_2$ directly, whilst the second pathway constitutes a reversible reaction between ONSCN and SCN^- to yield NO and an $(SCN)_2^-$ intermediate. The rate limiting step of the second pathway involves the reaction between $(SCN)_2^-$ and ONSCN, which could occur via S-nitrosation of $(SCN)_2^-$ by ONSCN or through a radical substitution mechanism. The third reaction pathway, which becomes significant at low thiocyanate concentrations, involves the formation of a previously unreported species, ONOSCN, via reaction between ONSCN and HOSCN, the latter being an intermediate in the hydrolysis of $(SCN)_2$. The proposed kinetic mechanism provides an excellent fit to the experimental measurements, and enables accurate modelling of the ONSCN decomposition reactions. Comparison of the HNO_2 and ONSCN decomposition kinetics showed that HNO_2 decomposition is the dominant NO_x formation pathway under conditions relevant to explosive sensitisation.

A quantum chemistry study was undertaken to determine the thermodynamic feasibility of the nitrosyl thiocyanate decomposition mechanism proposed on the basis of kinetic experiments. The procedure involved combining the results of accurate gas phase calculations, performed with the G3B3 and CBS-QB3 methods, with solvation free energies computed using continuum solvent models. Eight different procedures for calculating the solvation free energy were benchmarked against a set of six reactions with established reaction free energies, with the combination of the B3LYP/6-

31+G(d,p) method and the PCM solvation model with either UAHF or UFF atomic radii yielding the best results, with a mean absolute deviation on the order of 6 kJ mol^{-1}. The quantum chemistry results support the experimentally determined reaction mechanism, and confirmed the formation and subsequent decomposition of the previously unreported species, ONOSCN, to be thermodynamically feasible.

The solubility of nitric oxide in ammonium and sodium nitrate solutions was examined at temperatures ranging from 25 to 55 °C, at salt concentrations up to 7.5 and 10 mol L^{-1} for the sodium and ammonium salts, respectively. The solubility decreased significantly with increasing salt concentration, as predicted from the Sechenov equation. The enthalpy of solvation of NO decreased considerably with increasing salt concentration, indicating that the effect of temperature on the solubility diminishes with increasing salt concentration. The effect of sodium nitrate on NO solubility was significantly greater than that of ammonium nitrate, in agreement with previous literature results, which show that sodium ions have a much greater effect on gas solubility than ammonium ions. A model was developed to describe the solubility of NO as a function of salt concentration and temperature. The model predicted the solubility of NO in 13 mol L^{-1} NH$_4$NO$_3$ (as found in emulsion explosives) to be 5 times lower than in water at 25 °C, and largely independent of temperature.

A novel membrane inlet reactor was employed to examine the effect of ammonium and sodium nitrate concentrations on the decomposition equilibrium of nitrous acid. An increase in the observed equilibrium constant was recorded at low salt concentrations (up to 1 mol L^{-1}) owing to the initial rapid decline in the nitrate activity coefficient with increasing salt concentration, whilst a steady decline in the observed equilibrium

constant at high salt concentrations was attributed to the relative increase in the activity coefficients of NO and H^+ compared to that of HNO_2. Modelling of the activity coefficients of species involved in nitrous acid decomposition permitted extrapolation of the results to supersaturated solutions of ammonium nitrate relevant to emulsion explosives. Owing to cancellation effects among the activity coefficients of species involved in the decomposition equilibrium, the model predicts a similar aqueous NO concentration in concentrated salt solution to that observed in dilute acid. However, owing to the salting out effect, under the conditions of the present study, the equilibrium partial pressure of nitric oxide is approximately four times higher in concentrated ammonium nitrate compared to dilute acid solution.

A kinetic model was developed to predict the rate of N_2 and NO formation from the nitrosation of ammonia under conditions relevant to emulsion explosives. Experiments in ammonium nitrate solution showed that the model correctly predicts the rates of both N_2 and NO formation, including the catalytic effect of thiocyanate ions. The kinetic model was then employed to predict the amount of NO produced during the gassing of an emulsion explosive, and the results compared to laboratory measurements. Simulations showed that inclusion of sulfamate ions in the emulsion could significantly reduce the amount of NO formed, whilst addition of urea was predicted to have a negligible effect owing to its poor reactivity with nitrous acid. The levels of NO predicted by the model were similar to those observed experimentally, confirming nitrous acid decomposition as the sole source of NO_x during explosive sensitisation.

A common commercial chemical gassing technology involves sequential addition of concentrated acid and nitrite solutions to the explosive. Both experiments and

simulations showed that, provided the components required to effect nitrosation are well mixed into the explosive, nitric oxide constitutes less than 1 % of the reaction products. However, during large scale explosive sensitisation, inadequate mixing could lead to direct contact between the concentrated acid and nitrite solutions. Experiments showed that direct contact between concentrated acetic acid and sodium nitrite solutions results in rapid nitrous acid decomposition, with the stoichiometric amount of nitric oxide produced within 5 min. As such, direct contact between these solutions is the likely cause of visible NO_x emissions during explosive sensitisation. The amount of NO formed can be reduced by inclusion of a nitrous acid scavenger in the acid solution to convert nitrous acid into harmless N_2, however, owing to the rapid rate of nitrous acid decomposition in concentrated solutions, NO formation cannot be completely eliminated.