KINETICS OF THE TRAPPING REACTION OF NITRIC OXIDE WITH 3,5-DIBROMO-4-NITROSOBENZENE SULFONATE

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Overview

We have evaluated the reaction kinetics of trapping of toxic free radical nitric oxide (NO) by 3,5-dibromo-4-nitrosobenzene sulfonate (DBNBS) under acidic conditions at room temperature in batch experiments. Membrane inlet mass spectrometry (MIMS) served to quantify NO_x in aqueous solution directly and continuously from trapping reaction. The rate of trapping was found to be around 15000 times faster than the rate of generation of nitric oxide from the decomposition of nitrous acid with $k_{Trap} = 4.45 \times 10^{2}\ M^{-1}s^{-1}$ at 25 °C. The results here show that DBNBS is an efficient and fast NO scavenger that can potentially be applied in chemical system to reduce NO_x emissions.

1. Introduction

- Nitric oxide is a highly toxic free radical formed in several important chemical industrial processes. Small level of NO can affect human central nervous system as well respiratory and reproductive functions while exposure to high level of this gas can lead to asphyxiation and eventual death.
- The development of effective methods to scavenge this toxic gas is thus essential to minimise human exposure particularly in the work environment.
- In biological systems, nitric oxide plays an important modulatory role in many physiological and pathological processes. Biochemists employ spin trapping techniques to study the molecule whereby a spin trap binds to the free radical to form a stable adduct detectable by EPR.
- The NO spin traps employed by biochemists can ideally serve to control NO_x emissions from industrial processes producing NO_x.
- This project focuses on 3,5-dibromo-4-nitrosobenzene sulfonate (DBNBS) an aromatic nitroso spin trap which has been previously identified to trap successfully nitric oxide produced from the decomposition of sodium nitrite under acidic conditions.

2. Aims and Objectives

- Evaluate the kinetics of trapping of NO generated from the decomposition of nitrous acid, by DBNBS at room temperature.
- Use MIMS for on-line and real measurement of nitric oxide in solution.
- Define the mass transfer rate of NO from aqueous to gaseous phase.
- Determine DBNBS dimer–monomer equilibrium constant (to calculate the concentration of the monomer capable to trap NO) by UV-Vis spectrum analysis.

3. Experimental

Material

- DBNBS was synthesised according to the method of Kaur et al. (1981) that requires the presence of concentrated sulfuric acid as catalyst.
- NO was generated via the decomposition of nitrous acid at pH of 3.5.

Membrane inlet design

- Measurement of nitric oxide was performed by membrane inlet mass spectrometry (Figs. 1 & 2).
- The membrane probe made of 10 mm semi-permeable silastic tubing was attached to the capillary which connected the membrane to the vacuum inlet, leading to the ion source of the mass spectrometer.
- The inlet was immersed in the 10 mL reactor affording NO flux to diffuse across the membrane, connected to a capillary leading to a quadrupole mass spectrometer.
- The spectrometer monitored a mass-to-charge ratio, *m/z*, of 30.
- The MS capillary was heated to 200 °C to prevent condensation of water vapour.

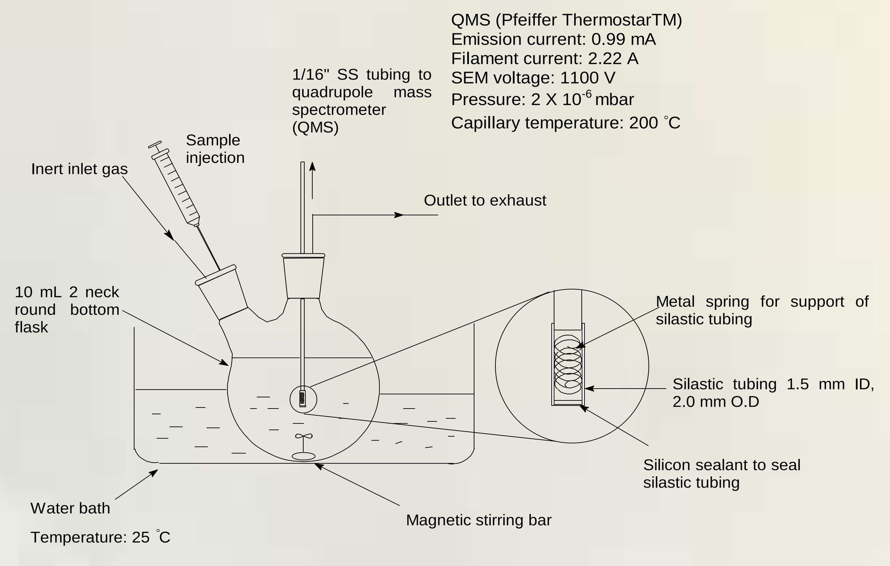

Fig 1. Diagram of the experimental setup for the measurement of NO from MIMS.

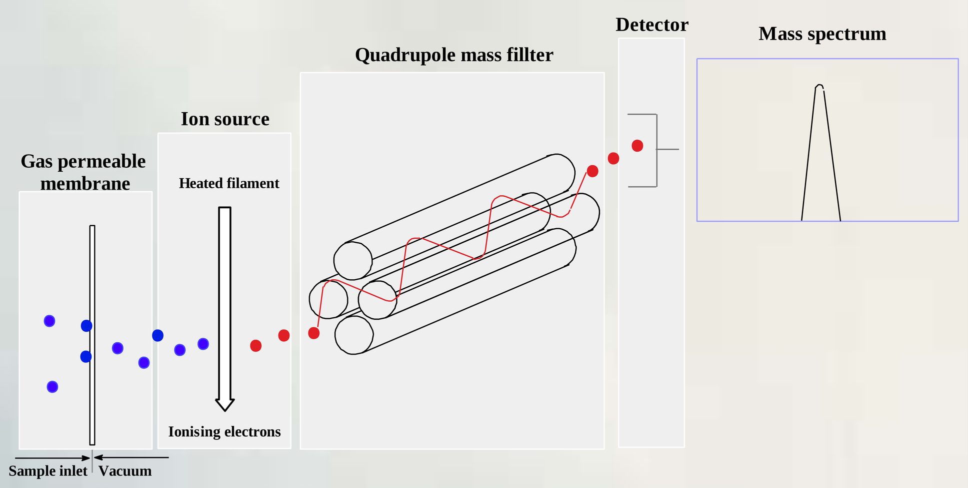

Fig 2. Schematic of MIMS system.

Calibration

- The membrane inlet mass spectrometer was calibrated by injecting solutions of known concentration of NO in the reaction vessel containing degassed water.
- The ion current was noted when it reached a maximum plateau.
- The data obtained were regressed yielding a $R^2 = 0.9972$ (Fig. 3).

Determination of equilibrium constant of DBNBS

- Samples for visible spectrum analysis were prepared by dissolving synthesised DBNBS (final concentration 0.05—8 mM monomer added) in distilled deionised water.
- Visible spectra (400-900 nm) were taken at 25 °C on a Varian Cary 50Scan UV-Visible spectrophotometer coupled with a single cell Peltier thermostated cell holder (Varian Inc.) using a sealed quartz cell (optical length 1 cm).

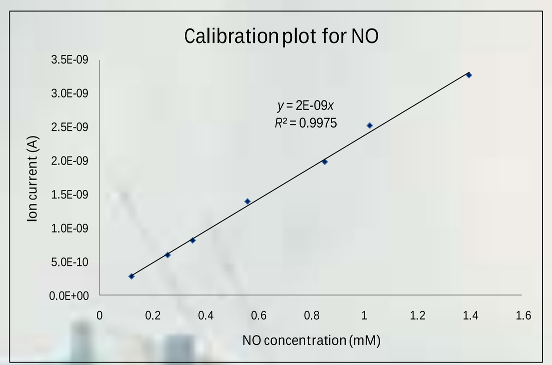

Fig 3. Ion current of the MIMS observed using solution dissolved NO of known concentrations.

4. Results and Discussion

A. Model for determining interphase (liquid to gas) mass transfer of nitric oxide

$$r_{MT} = k_{MT}([NO] - [NO]_{EQ}) \quad \text{Equation 1}$$

$$[NO]_{EQ} = k_{NO} P_{NO} \quad \text{Equation 2}$$

$[NO]_{EQ}$: equilibrium concentration of NO

$[NO]$: concentration of NO

P_{NO}: partial pressure of NO in equilibrium with solution

k_{MT}: mass transfer coefficient of NO

k_{NO}: Henry's law for nitric oxide

The model for determining the mass transfer provided an excellent fit to the measurement for the experiment with NO saturated solutions with $k_{MT} = 1.7 \times 10^{-3}\ s^{-1}$.

B. Reaction mechanism for nitrous acid decomposition

$$NO_2^- + H^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HNO_2 \quad (1)$$

$$2HNO_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} NO + NO_2 + H_2O \quad (2)$$

$$NO_2 + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HNO_2 + H^+ + NO_3^- \quad (3)$$

- A value of $k_3K_2^2$ of $2.6 \times 10^{-6}\ M^{-1}s^{-1}$ was found to fit the data well (Fig. 4).
- This value lies within the range of reported literature values of 2.8×10^{-6} and $2.4 \times 10^{-6}\ M^{-1}s^{-1}$ by Beake et al. (1995) and Schwarz et al. (1983) respectively.
- The results here show that MIMS provides a direct, continuous and quantitative measurement of nitric oxide over a long period of time.

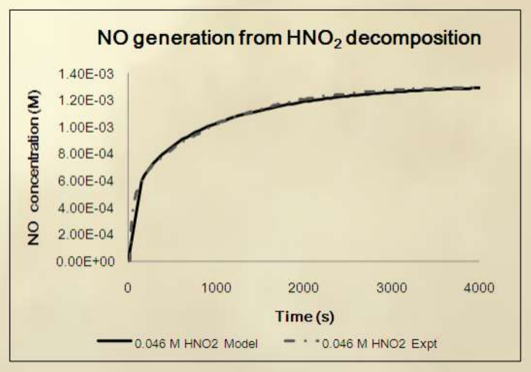

Fig 4. Generation of NO from the decomposition of HNO_2.

C. Model for NO generation by nitrous acid decomposition

Assumptions: Reaction 2 is at equilibrium and Reaction 3 is rate limiting

$$\frac{d[HNO_2]}{dt} = -\frac{3k_3K_2[HNO_2]^4}{[NO]^2}$$

$$\frac{d[NO]}{dt} = \underbrace{-\frac{2k_3K_2^2[HNO_2]^4}{[NO]_g^2}}_{\text{NO generation}} \underbrace{-\frac{K_{MT}([NO]_{aq} - (k_{NO}[NO]_g RT))}{V_{aq}}}_{\text{Mass transfer}}$$

$$\frac{d[NO]_g}{dt} = k_{MT}\left(\frac{[NO]_{aq} - k_{NO}RT[NO]_g}{V_g}\right)$$

D. Reaction mechanism for NO with DBNBS

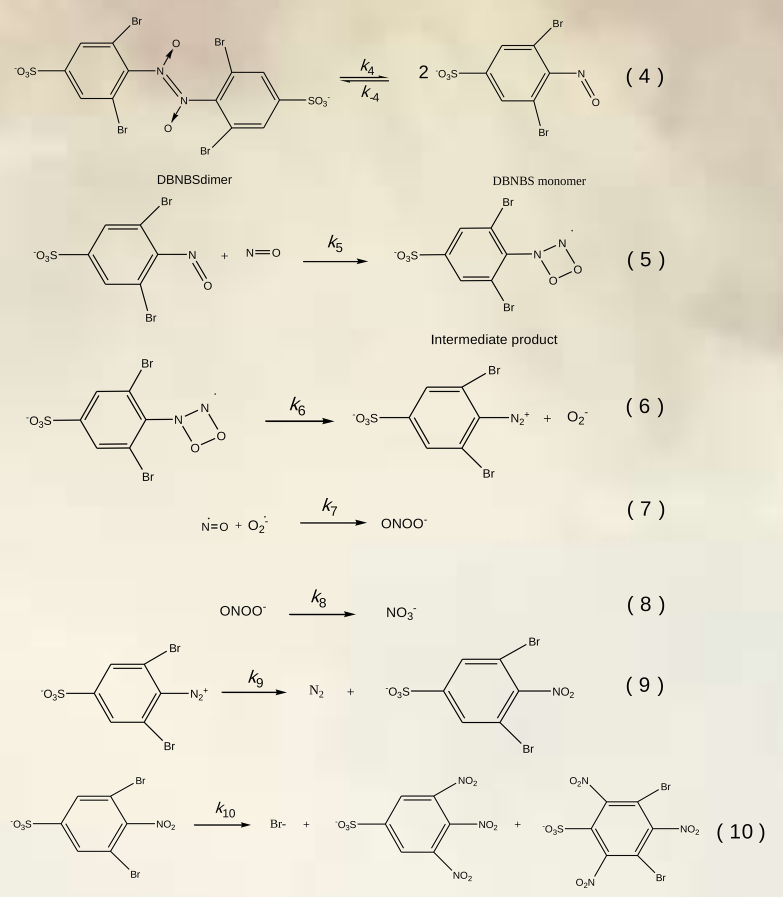

Fig 5. Proposed reaction mechanism for reaction of DBNBS with NO formed from nitrous acid decomposition

E. Determination of DBNBS dimer-monomer equilibrium

- The equilibrium was evaluated using Equation 3 assuming that the light adsorption at wavelength 760 nm is only due to the monomer.

$$\frac{D}{C_tL} = -\left(\frac{D^2}{C_tL^2}\right)\left(\frac{2}{K_C\varepsilon}\right) + \varepsilon \quad \text{Equation 3}$$

D: optical density

C_t: concentration of total nitroso compound (M)

ε: molar extinction coefficient per centimetre of cell length ($M^{-1}cm^{-1}$)

K_C: equilibrium constant (M) for reaction

- From Fig. 6, the linear plot gave $\varepsilon = 34.44 \pm 0.51\ M^{-1}cm^{-1}$ and $K_C = 1.29 \pm 0.03 \times 10^{-3}$ M.
- The value of K_C obtained at 25 °C is close to the value of 1.3×10^{-3} M reported by Ide et al. (1992).
- Majority of dissolved DBNBS is present in the dimeric form at room temperature (ca. 80% of 10 mM DBNBS).

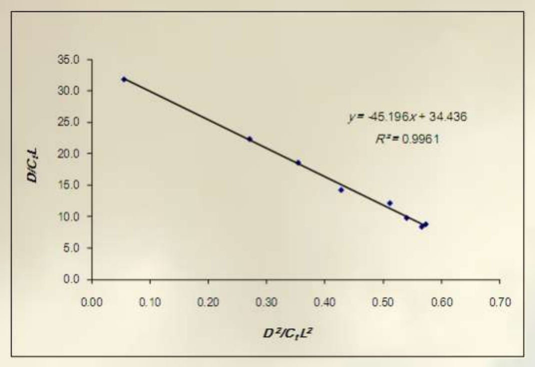

Fig 6. Plot of D/C_tL against D^2/C_tL^2 for determining DBNBS dimer-monomer equilibrium.

F. Model for trapping NO by DBNBS

To derive the rate law for the postulated scheme, the following approximation was considered: Reactions 6 & 7 are very rapid and the intermediate product and superoxide do not accumulate.

$$\frac{d[NO]}{dt} = -\frac{2k_3K_2^2[HNO_2]^4}{[NO]_{aq}^2} - \frac{k_{MT}([NO]_{aq} - (k_{NO}[NO]_g RT))}{V_{aq}} - 3k_5[DBNBS][NO] - k_7[NO][O_2^-]$$

$$\frac{d[HNO_2]}{dt} = -\frac{3k_3K_2[HNO_2]^4}{[NO]^2}$$

$$\frac{d[DBNBS]}{dt} = -k_5[DBNBS][NO] + k_4[Dimer] - k_{-4}[DBNBS]^2$$

$$\frac{d[O_2^-]}{dt} = -k_7[NO][O_2^-] + k_6[IP]$$

$$\frac{d[IP]}{dt} = -k_6[IP] + k_5[DBNBS][NO]$$

$$\frac{d[NO]_g}{dt} = k_{MT}\left(\frac{[NO]aq - k_{NO}RT[NO]_g}{V_g}\right)$$

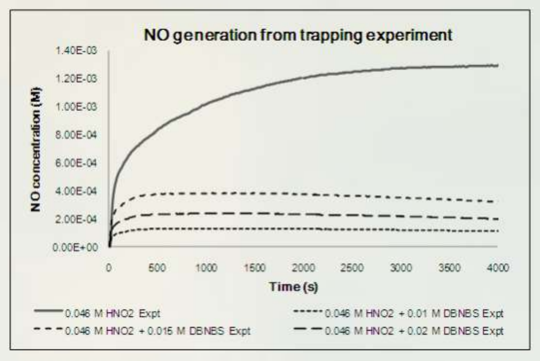

Fig 7. Generation of NO from the trapping experiment at different DBNBS concentrations.

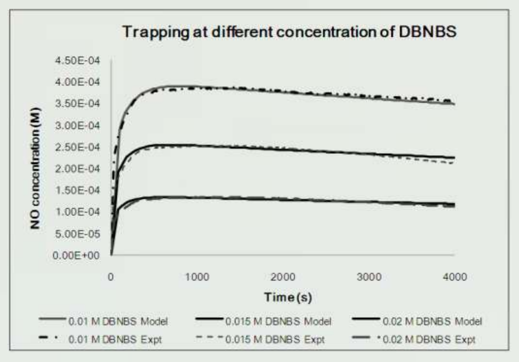

Fig 8. Fitting the proposed model to experimental measurements.

- The trapping of NO by DBNBS was modelled using Polymath based on the above reaction mechanism.
- Reactions 9 & 10 were excluded in the model since nitric oxide was not involved in these reactions.
- The model provided a good fit to the experimental data at different concentration of DBNBS employed (Fig. 8) with the rate constant for trapping NO; $k_{Trap} = 4.45 \times 10^{2}\ M^{-1}s^{-1}$ at 25 °C.
- The results showed that the rate of trapping was 15000 times faster than the rate of NO generation by nitrous acid decomposition.

5. Conclusion

Based on the kinetics results, DBNBS is an efficient and fast NO scavenger that can potentially be applied in chemical systems to reduce NO_x emissions.

6. Acknowledgement

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7. References

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