The formation of nitrosamines in the presence of NO\textsubscript{x} and O\textsubscript{2} under CO\textsubscript{2}-capture conditions

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Abstract

This case study demonstrates that piperazine, a secondary amine used in amine-based PCC formulations, reacts slowly with NO\textsubscript{x} in the presence of O\textsubscript{2} to form a nitrosamine derivative under conditions similar to those found in industrial amine-based post-combustion CO\textsubscript{2} capture processes. A gas stream consisting of 81.4 % N\textsubscript{2}, 12.8 % CO\textsubscript{2}, 0.8 % NO and 5.0 % O\textsubscript{2} flowing at 1.34 L/min through 200 g of 15 % wt aqueous solution of piperazine (in a water bath at 40 °C) was sampled at regular three hour intervals and analysed for the presence of N-nitrosopiperazine using direct infusion ESI-MS. Peaks due to the protonated forms of N-nitrosopiperazine (m/z 116), N-oxopiperazine or cationic 1-piperazinol (m/z 102), and piperazine nitramine (m/z 132) were detected after 7 hours. The structural identity of each of these species was confirmed using MS/MS experiments. The peak at m/z 116 increased relative to m/z 87 (protonated piperazine) during the course of the experiment, suggesting accumulation of nitrosamines over time.

Keywords: post combustion capture, chemical analysis, environment, pollution, nitrosamine

Introduction

The potential widespread application of post-combustion CO\textsubscript{2} capture (PCC) technology as part of a greenhouse gas mitigation solution for stationary power sources (eg. coal fired power stations) will lead to a large variety of amines being used as capture solvents. The entrainment of volatile amines and degradation products in the scrubbed flue gas, with subsequent release to the environment, is an issue that requires attention given the magnitude of potential PCC operations globally. To this end, important initial steps have been taken (Bråten \textit{et al.}, 2008; Stangeland and Shao, 2009) however, significant efforts in areas such as:

(i) understanding the photochemistry of slipped amines and degraded by-products, and their atmospheric half-lives, and
(ii) understanding the impact of slipped amines and degraded byproducts on the biosphere, eg. organism toxicity,

are warranted and necessary.

The reports by Braten \textit{et al.} (2008) and Stangeland and Shao (2009) clearly indicate that there is the potential for nitrosamine and nitramine generation during the utilisation of organic amines in a PCC process. Nitrosamines and other N-centred radicals are potentially hazardous to mammals and aquatic life-forms (Wang \textit{et al.}, 2002). In this study which is the first of its kind, we have undertaken

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experiments to confirm the presence of the N-nitrosamine and N-oxo derivatives of piperazine under typical process conditions.

Piperazine is a heterocyclic diamine with two secondary amine groups that is commonly found in commercial PCC formulations (Clossman et al., 2009; Freeman et al., 2009; Nainar and Veawab, 2009) and also finds use as a promoter of inorganic CO\textsubscript{2} capture reagents (Cullinane and Rochelle, 2004).

We have discovered that the experimental conditions under which these piperazine derivatives form are not dissimilar to the conditions found inside a typical CO\textsubscript{2} flue-gas absorption column e.g. P ~ 1 atm; gas composition 81.4 \% N\textsubscript{2}, 12.8 \% CO\textsubscript{2}, 0.8 \% NO and 5.0 \% O\textsubscript{2}; temperature = 60 °C. The principal differences between our experiments and those of a typical capture plant are:

(i) the absence of sorbent cycling, which is performed industrially to regenerate the parent amine from the carbamate derivative, and

(ii) elevated nitric oxide levels, used as a proxy for NO\textsubscript{x}, which is usually present at approximately 300-700 ppm in flue streams derived from black coal (Cottrell et al, 2009). Elevated levels of nitric oxide and nitrogen dioxide will simply accelerate the rate of formation of N-nitrosopiperazine.

Possible mechanisms for the formation of N-nitrosopiperazine which are relevant to PCC CO\textsubscript{2}-capture conditions are also discussed.

**Materials and Methods**

A diagram of the gas absorption apparatus is presented in Figure 1. All gases were purchased from BOC. The NO\textsubscript{x} was purchased as a 1 \% mixture in N\textsubscript{2}. A simulated flue gas stream consisting of 81.4 \% N\textsubscript{2}, 12.8 \% CO\textsubscript{2}, 0.8 \% NO (approx. 8000 ppm) and 5.0 \% O\textsubscript{2} was prepared using calibrated mass-flow controllers (Bronkhurst, all 0-1 L/min except 0-2 L/min CO\textsubscript{2}). The gas flow rate was set to 1.34 L/min. Appropriate measures (aluminium foil, opaque reaction and sample vessels) were adopted to exclude light from the reaction mixture. Flow was entrained through a 200 g mass of 15 \% wt aqueous solution of piperazine (Sigma, 99.8 \%) maintained at a constant temperature of 60 °C by a water bath (Techne Instruments). The reaction mixture was sampled at 3 hour intervals (T\textsub{tot} = 15 hrs). When necessary, the solution was stored overnight in a freezer (-16 °C). Each sample was analysed by using positive ion ESI-MS. The pH of the reaction mixture was also measured after sampling, using pH strips (Macherey-Nagel). In separate experiments undertaken to synthesise N-nitrosopiperazine in the lab, a 2 ml aliquot of aqueous 5 M NaNO\textsubscript{2} (Sigma) was added to 18 ml of 15 wt \% aqueous piperazine and the mixture incubated at 45 °C in a water bath (Techne Instruments) for one week; 30 wt \% solution of H\textsubscript{2}O\textsubscript{2} was added dropwise (final volume added = 1 ml) to 10 ml of 15 wt \% aqueous piperazine solution maintained at 4 °C by an ice bath. MS/MS spectra derived from these studies can be provided upon request.

All MS experiments were performed using a Waters Acquity HPLC-MS equipped with a T-wave cell. Water:acetonitrile was used as a solvent mobile phase, (solvent cluster peaks featuring CH\textsubscript{3}CN appear in resulting spectra). MS/MS experiments at unit mass resolution were used to confirm the structural assignments of the masses of interest. The collision gas was argon (99.999 \% purity, BOC). Spectra were averaged over many scans (in some cases > 100), particularly the MS/MS spectra of ions of low intensity.
Results

The pH of the solution exposed to the simulated flue gas did not fall below $9.0 \pm 0.5$ pH units for the full duration of the experiment (15 hours, 154.4 L $\text{CO}_2$ or 6.9 moles at standard temperature and pressure (STP), 9.65 L NO or 0.4 moles at STP). The initial pH of the unloaded solution was found to be close to 12.0 $\pm$ 0.5 pH units, and solution “acidification” was completed prior to taking the first sub-sample i.e. the pH had dropped to 9. The reaction mixture also turned pale yellow, characteristic of aqueous nitrite (see Figure 2). For comparison, an aqueous 15 wt % solution of piperazine was loaded with 4 moles of pure $\text{CO}_2$, but no colour change was observed. It is clear that the change in the mixture is due to the NO/O$_2$ content of the simulated flue gas, forming NO$_2^{-}$ (aq).

Figure 1. Schematic of the reactor used to expose amine solutions to synthetic flue gas.

Figure 2. Image of aqueous piperazine reaction mixtures (sub-sample of 200 g, 15 wt %) exposed to (left) 4 moles $\text{CO}_2$ and (right) simulated flue gas with oxygen.
The broad-scan \((m/z\ 50 – m/z\ 250)\) positive ion ESI-mass spectrum of a 15 wt % solution of piperazine exposed to simulated flue gas for 7 hours is presented in Figure 2. Peaks identified and labelled in the figure include \((H_2O)(CH_3CN)H^+\) (mobile phase solvent cluster), \((CH_3CN)Na^+\) or \(H_2NO_3^+\), \((CH_3CN)_2H^+\), PZH\(^+\), \((CH_3CN)_2Na^+\), PZ-OH\(^+\) (the N-oxide of piperazine), PZNOH\(^+\) (putative N-nitrosopiperazine), PZ-CO\(_2\)H\(^+_2\) (piperazine carbamic acid derivative) and PZ-NO\(_2\)H\(^+\) (piperazine nitramine). Protonated acetonitrile and other solvent cluster abundances are highly variable, but can be eliminated at higher curtain gas flow rates, however these conditions compromise the abundance of the piperazine derivatives of interest.

Broad-scan spectra obtained from samples exposed to the simulated flue gas for 3.5, 7.0 and 9.0 hrs respectively are presented Figure 3. There was no appreciable formation of N-nitrosopiperazine in samples \((t = 3.5\) hours, \(t = 14\) hours) exposed to a simulated flue gas without oxygen (composition 81.4 % N\(_2\), 17.8 % CO\(_2\), 0.8 % NO); these spectra can be provided upon request. The abundance of the peak at \(m/z\ 116\) (putative N-nitrosopiperazine) increases appreciably with time in the presence of oxygen, and a peak at \(m/z\ 145\) is also observed after 15 hrs, corresponding to protonated N,N'-dinitrosopiperazine. \(M/z\ 116\) is only barely detectable in the sample exposed to the simulated flue gas with no oxygen. The ratio ‘r’ of the ion current measured at \(m/z\ 116\) (protonated N-nitrosopiperazine) relative to the ion current measured at \(m/z\ 87\) (protonated piperazine) can be used to assess the increase of nitrosopiperazine relative to piperazine in the samples over the course of the experiment: \(t = 3.5\) hrs; \(r = 0.000\) hrs, \(t = 7.0\) hrs, \(r = 0.006\); \(t = 15\) hrs, \(r = 0.400\). For the sample exposed to flue gas without oxygen, \(t = 14\) hrs, \(r = 5.93 \times 10^{-5}\).

1.1 Protonated N-piperazine oxide / cationic 1-piperazinol

The low energy collision-induced dissociation (CID) spectrum of (putative) protonated N-piperazine oxide / cationic 1-piperazinol, a radical species, is presented in Figure 4. The spectrum was obtained by mass-selection of \(m/z\ 102\), a small but significant peak in the positive-ion broad scan spectrum of an aqueous 15 % wt solution of piperazine modified by exposure to simulated flue gas for 7 hours, and subsequently directly infused into the mass spectrometer at a flow rate of 50 µl/min. The
Figure 3. Broad-scan spectra of the aqueous piperazine reaction mixture after exposure to simulated flue gas for (1) $t = 3.5$ hours, (2) $t = 7$ hours, and (3) $t = 15$ hours. m/z 116, N-nitrosopiperazine, is labelled with an asterisk. N-nitrosamine can be seen to increase with time relative to the piperazine (m/z 87) peak.

The collision induced dissociation spectrum is dominated by the daughter ion at m/z 58, corresponding to loss of 44 mass units. Low energy rearrangement reactions and the expulsion of stable neutral molecules dominates the CID spectra at low energies. The nitrogen rule can be applied to eliminate the possibility of acetaldehyde loss i.e. molecules with an odd mass (in this case m/z 58-1H⁺ = 57 mass units) contain an odd number of nitrogen atoms. Other fragments include m/z 45 (protonated acetaldehyde), water loss (m/z 84), NO⁺ or protonated ethanimine (CH₂NH₂⁺, m/z 30), ethene or CO loss (m/z 74), and two distinct peaks at m/z 71 and m/z 72, likely to correspond to loss of HNO and NO⁺, although losses of aminoethane and formaldehyde cannot be ruled out. The weight of evidence in favour of the N-oxide of piperazine, a possible intermediate in the formation of N-nitrosopiperazine, is strong. There is also excellent correspondence between the CID spectrum of m/z 102 obtained from the solution exposed to simulated flue gas and m/z 102 generated by direct infusion of a piperazine solution incubated with NaNO₂ at 40 °C for 50 hours.

1.2 Protonated 1-nitrosopiperazine

The low energy CID spectrum of (putative) protonated 1-nitrosopiperazine (m/z 116) is presented in Figure 5. Loss of 30 (NO) and 31 (HNO) mass units dominate the spectrum, leaving little doubt that m/z 116 is indeed protonated nitrosopiperazine. The losses can be rationalised according to Scheme 1, with loss of 31 mass units resulting from protonation of the NO group, whereas protonation of either ring nitrogens leads to loss of NO⁺. Evidence that the nitrogen in the four position is protonated is the peak corresponding to loss of ammonia (17 mass units, m/z 99). The peaks at m/z 56, 57 originate from losses of methanimine from m/z 85, 86 respectively (refer to Scheme 1). The peak at m/z 30 (NO⁺) is likely to arise...
from charge-trapping upon dissociation of the parent ion, to produce neutral piperazine after rearrangement.

Although derived using different ionisation methods, there is excellent agreement between the electron ionisation mass spectrum of N-nitrosopiperazine (Linstrom and Mallard, 2009) and the ESI-mass spectrum presented in Figure 5.

Figure 5. The collision induced dissociation spectrum of protonated N-nitrosopiperazine.

Scheme 1. Fragmentations of N-nitrosopiperazine.
1.3 Protonated 1-nitropiperazine

A weak peak observed at \( m/z \) 132 was subjected to collision induced dissociation experiments. The resulting spectrum is presented in Figure 6. Interference from a sodiated species, also with \( m/z \) 132, is apparent through daughter peaks at \( m/z \) 23 (\( \text{Na}^+ \)) and \( m/z \) 91. The latter results from loss of \( \text{CH}_3\text{CN} \), and is the base peak in the CID spectrum. Unfortunately, the unidentified contaminant is more abundant than the ion of interest. Peaks which confirm the existence of the nitramine derivative of PZ (\( \text{HNC}_3\text{H}_8\text{N-ONO}^+ \)) include the loss of \( \text{NO}^• \) (\( m/z \) 102), loss of \( \text{NO}_2^• \) (\( m/z \) 86) and loss of \( \text{HNO}_2 \) (\( m/z \) 85). The loss of water (\( m/z \) 114) could be attributed to either the contaminant or protonated 1-nitropiperazine.

\[ \text{HONO} \xrightarrow{+\text{H}^+} \text{H}_2\text{ONO}_2^+ \xrightarrow{-\text{H}_2\text{O}} \text{NO}^+ \xrightarrow{+\text{PZ}} \text{PZ-NO} \]

![Figure 6. The collision induced dissociation spectrum of protonated N-nitropiperazine.](image)

Discussion

It is apparent from the colour of the resulting reaction mixture that aqueous nitrite is formed after bubbling the simulated flue gas through the aqueous piperazine solution. The actual mechanism of nitrosation is poorly understood, and a number of species have been identified with different degrees of nitrosating potential, including \( \text{N}_2\text{O}_3 \), \( \text{N}_2\text{O}_4 \), \( \text{HOONO} \) (peroxynitrous acid), \( \text{OONO} \) radical and peroxyxynitrous anion \( \text{OONO}^- \) (Hughes 1999; Hughes 2009; Goldtein and Czapski 1995). \( \text{NO}_2 \) is only a very small percentage of \( \text{NO}_x \) gas, and the slow rate of N-nitrosopiperazine formation suggests \( \text{NO}_2 \) plays a role in PZ-nitrosation. A widely accepted mechanism catalysed by protons (low pH) involves nitrous acid:

However it is doubtful such a mechanism would apply at the high pH levels of our experiment, as the pKa value for HONO is 3.25 (Lide, 2009b), so it will exist in the anionic form \( \text{NO}_2^- \) at pH 9 and above. Piperazine itself will exist in both protonated and de-protonated forms at the pH values measured in our
experiment ($pK_a$ PZ = 9.73, Lide 2009a). In this study, there are four important points to note when considering any nitrosation mechanism of PZ under CO$_2$ capture conditions:

(i) the pH of the solution did not change dramatically during the course of the experiment, even though $> 1200$ L of acid gas was bubbled through the system.
(ii) the removal of oxygen from the flue gas had a noticeable inhibitory effect on the rate of N-nitrosopiperezine formation
(iii) the N-oxide derivative of piperazine was detected, which is potentially an intermediate in the formation of N-nitrosopiperezine, and
(iv) N$_2$O$_3$ hydrolys under basic conditions (Goldstein and Czapski, 1995)

The critical role of oxygen in enhancing N-nitrosamine formation points to (i) a peroxynitrous species, (ii) solution oxidation of NO to NO$_2$, possibly followed by the reaction $2$NO$_2$ $\rightarrow$ N$_2$O$_4$, which then proceeds to oxidise piperazine. Clearly, the chemistry is quite complex. Further, to this point the effect of CO$_2$ has not been considered; CO$_2$ reacts with PZ in aqueous solutions to form both a carbamate, and a dicarbamate, and both derivatives will hydrolyse to some extent to regenerate PZ and yield bicarbonate:

$$
\text{PZ} \xrightarrow{\text{CO}_2/\text{base}} \text{PZ-CO}_2^- \xrightarrow{\text{CO}_2/\text{base}} \text{O}_2\text{C-PZ-CO}_2^- \xrightarrow{\text{base-H}^+} \text{PZ} + \text{bicarbonate}
$$

This is the CO$_2$ capture process chemistry which is intended for PZ when it is deployed as a PCC solvent. What remains unclear is whether displacement reactions also contribute to N-nitrosamine formation via:

$$
PZ-CO_2^- + \text{HONO} \rightarrow PZ-NO + HCO_3^-$$
$$PZ-CO_2H + \text{ONO}^- \rightarrow PZ-NO + HCO_3^-$$

NO$_2^-$, the conjugate base of the reducing acid HONO, will only be weakly oxidising, however gaseous NO$_2$ is quite corrosive and can be considered a strong oxidant. A peroxynitrite species or N$_2$O$_4$ is suspected to be responsible for the N-oxidation of piperazine. Once the radical N-oxide of piperazine is formed, further reaction with a nitrosating species or NO in an addition fashion yields PZ-ONO, as detected in the piperazine solution exposed to simulated flue gas (Figure 6). We note that while NO$_x$ gas oxidises PZ to the N-oxide species, H$_2$O$_2$ added dropwise results mostly in formation of a hydroxyl species:
It is known that OH radicals are formed in solution upon addition of H₂O₂, and this result suggests secondary OH species are not responsible for generation of N-oxopiperazine.

In order to confirm the proposed MS/MS fragmentation schemes and the true mechanisms involved in the aqueous formation of N-nitrosopiperazine, extensive labelling studies are required, and/or ab initio computations. These experiments are currently underway in our laboratory, as well as HPLC-MS method development for quantification.

Conclusions

The formation of N-nitrosopiperazine at high pH and low temperature (60 °C) in the presence of oxygen and nitric oxide has been confirmed using direct infusion positive ion ESI-MS/MS experiments. Nitrosamine formation may be problematic for secondary alkanolamine sorbents such as piperazine, diethanolamine, piperidine and their derivatives, as well as in significantly degraded PCC capture solvents of primary amines where polymerisation to secondary species may have occurred.

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References


