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Nitrosamine Formation Mechanism in Amine-Based CO₂ Capture: Experimental Validation

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Abstract

This work presents qualitative experimental validation of nitrosamine mechanism previously proposed by our group which stated that, without nitrogen dioxide (NO₂), nitrosamine could form from secondary amine reaction with only nitric oxide (NO), oxygen (O₂), sulfur dioxide (SO₂) and carbon dioxide (CO₂). Experimentally, N-nitrosodiethylamine (NDEA) from diethylamine reaction was confirmed by detection in both liquid and gas phases. If diethylamine could form NDEA with only NO, O₂ SO₂ and CO₂, other secondary amines used more commercially (e.g. piperazine (PZ) and its derivatives and diethanolamine) in the capture of CO₂ could potentially form their corresponding nitrosamines under similar conditions.

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1. Introduction

The classic reaction schemes for nitrosamine formation under acidic conditions involve formation of nitrosonium ion (NO⁺), a nitrosating agent from NO-Y in aqueous solution derived from nitrogen dioxide (NO₂) (where Y can be a variety of anions including SCN⁻, I⁻, Br⁻, and Cl⁻) [1]. However, with the shortage of proton (H⁺)
in an amine-based CO₂ capture environment, the formation of NO⁺ via this mechanism is limited, and thus difficult to proceed to react with the amine to form nitrosamine since nitrosamine formation in post-combustion amine-based CO₂ capture occurs under basic conditions. In addition, the majority of the components of NOx (100-300 ppmv) in flue gas is NO (~95%) with nitrogen dioxide (NO₂) being ~5% which mostly can be removed during the gas preconditioning process before the flue gas enters the amine scrubbing plant. Despite the fact that the amount of NO₂ (0-5ppm) is very small compared to NO (0-100ppm) in the CO₂ capture plant system, the formation of nitrosamine has been reported, in some cases, with the complete absence of NO₂ [2, 3]. Our previous work [4] has proposed the formation mechanism of nitrosamine under CO₂ capture conditions with the nitrosating process being generated only from NO, O₂, CO₂ and SO₂ (e.g. NO₂-CO₂⁻, NO₂-SO₂⁻, and NO₂-SO₃⁻). The mechanisms were deemed possible based on computational simulation and potential energy surface (PES) analysis. The mechanism was based on formation of nitrosamine from the reaction of nitric oxide (NO) with amine in the presence of O₂, SO₂ and CO₂. Therefore, this study was carried out to experimentally validate this mechanism hypothesis. The experimental validation was carried out to qualitatively validate the proposed mechanisms derived from the simulation work, using 2 kmol/m³ diethylamine (DEA) and NO, SO₂ and O₂ reacting at the desorber temperature of 393 K under conditions of no CO₂ loading and with lean and rich CO₂ loadings. The detection and identification of NDEA in bulk liquid and off-gas were used to confirm and validate the proposed mechanisms. In the tests, if analysis of test samples showed that NDEA was formed, then the mechanism was deemed valid. A specific reaction of DEA with NO, O₂ and SO₂ forming NDEA is given in Eq (1).

\[ \text{Diethylanine} + \text{NO} + \text{O}_2 + \text{SO}_2 \rightarrow \text{Nitrosodihydrilamine (NDEA)} \]  

2. Experiments

2.1 Chemicals and Equipment

Concentrated diethylanine (DEA, 99 % reagent grade) was used to prepare 2 kmol/m³ aqueous solution with deionized water and confirmed by titration with standard hydrochloric acid (HCl) of 1 N with methyl orange indicator. Both HCl and DEA were obtained from Fisher Scientific, Ontario, Canada. A research grade carbon dioxide (CO₂) cylinder was used for CO₂ loaded experiments while simulated feed gas used was composed of 100 ppm NO and 200 ppm SO₂ (N₂ balance) mixed with 100% oxygen (O₂). All gas cylinders were supplied by Praxair, Regina, Canada. The reaction for formation of nitrosamine was carried out using a 0.6 L stainless steel reactor (model 4560, Parr Instrument Co., Moline, IL). An electrical heating jacket supplying heat to the reactor was regulated by a temperature-speed controller (Model 4836, Parr Instrument Co., Moline, IL) of ±0.1 % accuracy. The same controller was also used to control and monitor the temperature of the solution mixture measured by a J-type thermocouple. The system pressure inside of the reactor was also monitored by the controller using a pressure transducer.

Gas chromatograph-mass selective detector (GC-MSD, model 6890-5073) supplied by Hewlett-Packard, Canada was used for analysis of nitrosamine in liquid and gas samples. The GC column was RTX-5 Aminex with the dimension of 30 mm-length x 250 mm-i.d. x 0.25 mm-film thickness packed with 5% diphenyl and 95% dimethyl siloxane (Chromatographic Specialties, Ontario, Canada). An autosampler/autoinjector (model 7683, Hewlett-Packard, Canada) with reproducibility of 0.3 % relative standard deviation (RSD) in terms of peak area percentage was used for sample injection. Ultra high purity grade helium (He, UHP) from Praxair, Regina, Canada was used as the carrier gas. Sample preconcentration based solid phase extraction (SPE) was also used prior to GC-MS analysis in order to ensure a clear visualization of NDEA using LiChrolut EN 40 SPE cartridge (120 μm particle size of 200 mg in 3 ml standard tube, Millipore (Canada) Ltd, Ontario, Canada). The extraction conditions, modified from a literature [5] used acetonitrile and ethyl acetate-acetonitrile mixture all purchased from Sigma Aldrich, Canada, to precondition and elute NDEA from the cartridge, respectively.
2.2 Experimental Run

Three test conditions were used to validate the mechanism. The tests were done using a fixed 2 M concentration of diethylamine solution. Feed pressure of O₂ and mixed gases composed of NO and SO₂ (N₂ balance) were fixed respectively at 14 and 28 psi. The temperature of 120°C was used for all tests. CO₂ loading was varied from none (0) to lean (0.23 mol CO₂/mol amine) and rich (0.64 mol CO₂/mol amine) conditions. For a typical run, 0.45 L of 2 M diethylamine solution was loaded into the reactor vessel. The reactor was assembled and connected to the temperature speed controller. The amine solution was simultaneously stirred at a speed of 500 rpm and heated to 120°C typical of desorber conditions. A few minutes were allowed to stabilize the solution temperature at which point the reactor pressure due to water vapor was approximately 60 psi. O₂ regulated at 14 psi in its cylinder was then introduced into the solution by opening the gas inlet valve of the reactor. Additional 28 psi of mixed NO and SO₂ (N₂ balance) from a separate cylinder was subsequently fed in to the reactor. Total pressure at the 0 reaction time was therefore the sum of water vapor, 14 psi of O₂, and 28 psi of NO+SO₂+N₂. For runs with CO₂, prior to the experiment, diethylamine was preloaded with the desired CO₂ loading using a 100% CO₂ cylinder. The exact loading was measured by titration of a 2 mL sample with standard 1 N HCl solution using methyl orange indicator. Liberated CO₂ was collected in a displacement mixture of NaCl, NaHCO₃, and methyl orange. CO₂ loading was calculated on the basis of mol CO₂ per mol amine. The remaining procedures were then followed as in non-CO₂ runs. The reaction was conducted for 2 weeks while reactor liquid samples were taken every day for analysis of NDEA. Collection of gas sample (i.e. reactor head space) was also carried out at the very end of the experiment. To collect a sample, the reactor gas outlet valve connected to the inlet of the condensation tube immersed in an iced bath in the impinger system was opened. N₂ was used at a regulated pressure at the reactor gas inlet to help flush out the off-gas above the amine liquid. Approximately 30 minutes were allowed during the off-gas collection process before the valves were shut off which also ended the experiment. Liquid and gas samples were sent for analysis using SPE technique previously described for pre-concentration. GC-MS was then used for separation and detection of NDEA in all samples.

3. Results and Discussion

3.1 Liquid phase formation of NDEA

The initial run involving the reaction of diethylamine with NO, O₂ and SO₂ but without CO₂ was used to check for NDEA formation. The day 1 sample collected from such a reaction was initially used to validate NDEA peak obtained from GC-MS analysis. Figure 1 shows SPE extracted samples peaks with NDEA peak labelled at approximately 4.4 minutes. NDEA peak identified in Figure 1 was confirmed by its mass spectrum analysis which produced over 90% match quality with NIST standard compound library. A comparison with NDEA standard injection was also carried out with the result being given in Figure 2. It is clear from the Figure that NDEA in the sample has the same retention same time as that of the NDEA standard, thus confirming that the peak identity from the sample as NDEA. Samples collected on day 2 to 5 were also analyzed for NDEA which their GC chromatograms were also plotted together in Figure 3 with day 1 sample. It is clear that without NO₂, NDEA could be generated by only NO, SO₂ and O₂. Although, quantitative analysis was not carried out. Comparison of sample collected daily clearly showed an increasing trend of peak size of NDEA as the reaction proceeded forward. This can actually confirm that NDEA could be formed in liquid phase even if NO, O₂ and SO₂ were only present in the reaction system. The same phenomenon should also occur with those secondary amines commonly used in CO₂ capture process including piperazine (PZ) and its derivatives and diethanolamine.
Fig. 1. GC Chromatogram of 1 day sample (2 M diethylamine, 14 psi O₂, 28 psi mixed NO and SO₂ (N₂ balance), and 120°C)

Fig. 2. Overlay of GC chromatograms of 1 day sample and standard NDEA (2 M diethylamine, 14 psi O₂, 28 psi mixed NO and SO₂ (N₂ balance), and 120°C)

Fig. 3. Overlay of GC chromatograms of NDEA samples from various days (2 M diethylamine, 14 psi O₂, 28 psi mixed NO and SO₂ (N₂ balance), and 120°C)

CO₂ was also used to evaluate its effect on the formation of NDEA from 2 kmol/m³ DEA. Lean and rich loading conditions respectively set at 0.23 and 0.64 mol CO₂/mol amine were also used. Figure 4 shows the formation of NDEA in the liquid phase at 0.23 and 0.64 CO₂ loading conditions. NDEA formation generated from runs without CO₂ was also given in the same figure. It is evident from GC analysis that NDEA was still detected under both lean and rich CO₂ conditions. It should be noted that CO₂ however, showed a mild effect in inhibiting amine degradation if co-existing with other flue gas impurities (e.g. O₂, SO₂ and NO), which also led to a decrease in the extent of
NDEA formation. Although quantitative analysis was not performed, the relative concentration of NDEA based on GC-MS peak size suggested a mild effect of CO$_2$ in inhibiting amine degradation in loaded amine samples. Judging from size of NDEA peak alone, the results implied that if the capture plant operated with a proper control of lean and rich CO$_2$ loading. This effect having been observed already in many degradation works previously done by our research group and possibly, could be used to help control nitrosamine formation while the capture plant is being operated.

![Image: GC chromatograms of NDEA samples from 3 and 5 day samples (2 M diethylamine, 14 psi O$_2$, 28 psi mixed NO and SO$_2$ (N$_2$ balance), 120°C, with 0, 0.23 (lean), and 0.64 (rich) CO$_2$ loadings)](image)

**Fig. 4.** GC chromatograms of NDEA samples from 3 and 5 day samples (2 M diethylamine, 14 psi O$_2$, 28 psi mixed NO and SO$_2$ (N$_2$ balance), 120°C, with 0, 0.23 (lean), and 0.64 (rich) CO$_2$ loadings)

### 3.2 Gas phase formation of NDEA

The gas sample was collected on the last day of the experiment. From the run without CO$_2$, 2 impingers were set up one after the other to ensure complete capture of NDEA from the gas sample. Figure 5 shows GC chromatograms of gas samples obtained from impinger 1 and 2, respectively. Being a volatile nitrosamine, NDEA likely existed in gas phase which was clearly detected in both impinger samples in this study. In addition, other gaseous products formed from the reaction were also present in the gas sample some of which were identified by the MS. Similar effect of CO$_2$ at 0.23 and 0.64 mol/mol amine seen earlier in the liquid samples could also be observed in gas phase analysis. Though not quantified directly, NDEA from run without CO$_2$ produced relatively bigger and broader peak compared to both runs with lean and rich CO$_2$ loadings as seen in Figure 6. Similar to liquid sample analysis, CO$_2$ co-existence with other impurities helped to reduce NDEA formation in the liquid phase, and thus reduced its emissions into the gas phase. The results from gas sample analysis also confirmed the existence of NDEA derived from the reaction of DEA with NO, O$_2$, SO$_2$ and CO$_2$.

Based on the results obtained from this study, it was proven that without NO$_2$, NDEA could be from in the presence of only NO, O$_2$, SO$_2$, and CO$_2$. NDEA was confirmed to form and can exist in both the bulk liquid and gas phases. Lean and rich CO$_2$ loading conditions were also found to reduce NDEA formation from the reaction. If diethylamine could form NDEA with only NO, O$_2$, SO$_2$ and CO$_2$, other secondary amines used more commercially in the capture of CO$_2$ could potentially form their corresponding nitrosamines under the same conditions.

![Image: NDEA and other gas products found in gas samples (2 M diethylamine, 14 psi O$_2$, 28 psi mixed NO and SO$_2$ (N$_2$ balance), and 120°C)](image)

**Fig. 5.** NDEA and other gas products found in gas samples (2 M diethylamine, 14 psi O$_2$, 28 psi mixed NO and SO$_2$ (N$_2$ balance), and 120°C)
4. Conclusions

The mechanism of nitrosamine formation from reaction of NO and O\textsubscript{2} with amine in the presence of SO\textsubscript{2} and CO\textsubscript{2} has been validated qualitatively. NDEA was confirmed to form and can exist in both bulk liquid and gas phases under the reaction system containing NO, O\textsubscript{2}, SO\textsubscript{2}, CO\textsubscript{2} and diethylamine under CO\textsubscript{2} capture conditions. Lean and rich CO\textsubscript{2} loading conditions were also found to reduce NDEA formation from the reaction when CO\textsubscript{2} co-existed with other flue gas impurities. If diethylamine could form NDEA with NO and O\textsubscript{2}, then other secondary amines could potentially form their corresponding nitrosamines under the same conditions.

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