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## Nitrosamine Formation Mechanism in Amine-Based CO<sub>2</sub> 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 (NO<sub>2</sub>), nitrosamine could form from secondary amine reaction with only nitric oxide (NO), oxygen (O<sub>2</sub>), sulfur dioxide (SO<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>). 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, O<sub>2</sub>, SO<sub>2</sub> and CO<sub>2</sub>, other secondary amines used more commercially (e.g. piperazine (PZ) and its derivatives and diethanolamine) in the capture of CO<sub>2</sub> could potentially form their corresponding nitrosamines under similar conditions.

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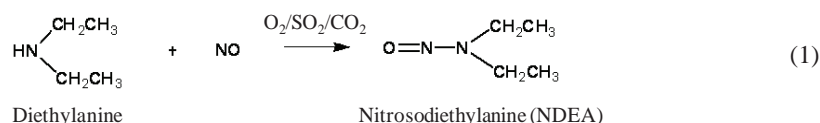
**Keywords:** Nitrosamine, CO<sub>2</sub> capture, Amine, Mechanism

### 1. Introduction

The classic reaction schemes for nitrosamine formation under acidic conditions involve formation of nitrosonium ion (NO<sup>+</sup>), a nitrosating agent from NO-Y in aqueous solution derived from nitrogen dioxide (NO<sub>2</sub>) (where Y can be a variety of anions including SCN<sup>-</sup>, I<sup>-</sup>, Br<sup>-</sup>, and Cl<sup>-</sup>) [1]. However, with the shortage of proton (H<sup>+</sup>)

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in an amine-based CO<sub>2</sub> capture environment, the formation of NO<sup>+</sup> 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 CO<sub>2</sub> capture occurs under basic conditions. In addition, the majority of the components of NO<sub>x</sub> (100-300 ppmv) in flue gas is NO (~95%) with nitrogen dioxide (NO<sub>2</sub>) 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 NO<sub>2</sub> (0-5ppm) is very small compared to NO (0-100ppm) in the CO<sub>2</sub> capture plant system, the formation of nitrosamine has been reported, in some cases, with the complete absence of NO<sub>2</sub> [2, 3]. Our previous work [4] has proposed the formation mechanism of nitrosamine under CO<sub>2</sub> capture conditions with the nitrosating process being generated only from NO, O<sub>2</sub>, CO<sub>2</sub> and SO<sub>2</sub> (e.g. NO<sub>2</sub>-CO<sub>2</sub><sup>-</sup>, NO<sub>2</sub>-SO<sub>2</sub><sup>-</sup>, and NO<sub>2</sub>-SO<sub>3</sub><sup>-</sup>). 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 O<sub>2</sub>, SO<sub>2</sub> and CO<sub>2</sub>. 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/m<sup>3</sup> diethylamine (DEA) and NO, SO<sub>2</sub> and O<sub>2</sub> reacting at the desorber temperature of 393 K under conditions of no CO<sub>2</sub> loading and with lean and rich CO<sub>2</sub> 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, O<sub>2</sub> and SO<sub>2</sub> forming NDEA is given in Eq (1).



## 2. Experiments

### 2.1 Chemicals and Equipment

Concentrated diethylamine (DEA, 99 % reagent grade) was used to prepare 2 kmol/m<sup>3</sup> 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 (CO<sub>2</sub>) cylinder was used for CO<sub>2</sub> loaded experiments while simulated feed gas used was composed of 100 ppm NO and 200 ppm SO<sub>2</sub> (N<sub>2</sub> balance) mixed with 100% oxygen (O<sub>2</sub>). 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 Amine 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.

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