Computational analysis of Nitrosamine Formation during Amine-Based CO\textsubscript{2} Capture process with different Groups of Nitrosating Agents (NO-X)

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1. Introduction

In an amine-based CO\textsubscript{2} capture from a coal-fired power plant, nitrosamines can be generated as a result of the reaction between impurities such as NOx (an example of a nitrosating agent) in the flue gas with amine solutions in the absorption column. There is the potential that the nitrosamines can be emitted to the atmosphere if adequate control measures are not put in place. As is well known, all amines types (i.e. primary, secondary, and tertiary) can react with nitrosating agents. However, the nitrosamine generated from primary amines (RNH\textsubscript{2}) will decompose to generate N\textsubscript{2} while the tertiary amine (R\textsubscript{3}N) is degraded when it reacts with nitrosating agents. Only secondary amines (R\textsubscript{2}NH) can generate stable nitrosamine products. That is why attention is focused on secondary amines such as DMA, PZ and MOR in nitrosamine studies. In the last few years, there has been a lot of interest in reactions for nitrosamine formation with most nitrosating agents. Nitrosating agents can be categorized into two major groups: NO\textsubscript{2} related agents, and NO derivatives (NO-X). NO\textsubscript{2} and N\textsubscript{2}O\textsubscript{4} belong to the first group while NO, N\textsubscript{2}O\textsubscript{3}, NOY, HNO\textsubscript{2}, NO\textsuperscript{+} and NO\textsuperscript{-2} belong to the second group (which can simply be written as NO-X). There are two important steps in the reaction pathway of NO-X nitrosation, N-NO bond generation and H transfer. Current studies show that the first step is N-NO bond generation before H transfer with nitrosating agents. However, it may also be possible for nitrosation to occur with H transfer occurring before N-NO bond generation depending on the prevailing circumstance. Also, it has been observed from actual process operation that even if all of NO\textsubscript{2} is removed from flue gas before entering the amine CO\textsubscript{2} capture absorber column, trace amount of nitrosamines can still be detected in the absorber offgas. The circumstance for NO-induced formation of nitrosamine has not yet been elucidated in the literature. Furthermore, the role that CO\textsubscript{2} plays in the nitrosation process is not yet clear. While there are indications

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that it can act as catalyst to speed up nitrosation, there are contradictory indications that it can also act as an inhibitor. This study uses a computational analysis approach to investigate the circumstances by which H transfer step can occur before N-NO bond generation in NO-X nitrosation of DMA and vice versa as well as conditions by which NO can induce the formation of nitrosamine. In addition, it explores the inhibition characteristics of CO$_2$ in nitrosamine formation. Computational simulations were performed on 15 different nitrosamines (NDMA) with a variety of NO-X-type nitrosating agents with the calculation of the reaction enthalpies and free energies.

2. Computational Procedure

The reaction mechanisms and pathways of NDMA formation with NO-X were proposed using the typical scheme: R$_1$R$_2$NH + NO-X $\rightarrow$ R$_1$R$_2$NNO + HX. All the calculations were completed with the Gaussian 03 program package. The nitrosation reactions of NDMA generation was investigated using the B3LYP[1] (Becke’s three-parameter nonlocal exchange functional with the correlation functional of Lee, et al. [2]) method, with DFT (density functional theory) method.[3] The basis set was 6-311+G(d,p)[4]. The structures of the reactants, products, intermediates, and transitions states were fully optimized with HF/6-311+G(d,p). Vibrational frequencies were calculated of the 15 nitrosamines as simulative results, as a reference for FT-IR experimental tests. Based on the optimized geometries with HF/6-311+G(d,p) level, the single-point energy of each stationary point was obtained with B3LYP method, labelled as B3LYP/6-311+G(d,p) //HF/6-311+G(d,p) with the code “freq”. As the nitrosation reactions take place in aqueous solution, the solvent effect of water was taken into account. On the basis of optimized geometries, the single-point energy calculation was carried out with CPCM (conductor-like polarizable continuum model) at the B3LYP/6-311+G(d,p) level.

3. Results

The energy diagrams of NDMA formation with 6 different agents (NO-X) are plotted and categorized into two groups. Based on the potential energy surface (PES) studies and transition state calculation, a key step is H transfer which possesses higher activation energy. It is only after the H transfer step has occurred that nitrosation can be completed irreversibly. The results also show that in an environment of weak proton affinity, N-N bond addition occurs before proton transfer. However, with strong proton affinity, proton transfer occurs before N-NO bond generation with a typical structure of 6-atom-ring. It is possible that with CO$_2$ in the liquid amine in the desorber, NO$_2$ can pair with the CO$_2$ to constitute a nitrosating agent NO$_2$-CO$_2$. Therefore, if there is limited CO$_2$ in the liquid amine (low CO$_2$ loading), there is free secondary amine (R$_1$R$_2$NH) left to react with the NO$_2$-CO$_2$ via mechanism Figs 1 and 2 to generate nitrosamine and bicarbonate (HCO$_3^-$) ion. This appears to be the catalytic role of CO$_2$ for formation of nitrosamine. It is interesting to observe that the same mechanism can be used to control nitrosamine formation. It is seen that an increase in CO$_2$ loading will reduce the availability of free secondary amine thereby resulting in less NO$_2$-CO$_2$ induced nitrosation to form nitrosamines. This mechanism also explains why it appears NO can induce the formation of nitrosamine. It appears that NO in the gas is oxidized with O$_2$ to NO$_2$ and then converted to NO$_2$-CO$_2$ in the liquid phase.

\[(CH_3)_2N + NO_2 \rightarrow (CH_3)_2N-NO_2\]  \hspace{1cm} (3)

\[NO + O_3 \rightarrow NO_2 + O_2\] \hspace{1cm} (4)

References


Fig. 1: Proposed mechanism of nitrosamine formation for ONOCO$_2^-$ (Proton transfer before bond formation)

Fig. 2: The PES diagram for the NDMA formation (DMA + NO$_2^-$CO$_2^-$)