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A study of thermal degradation of different amines and their resulting degradation products

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1. Introduction

For global CO₂-capture based on absorption the scale of solvent use will be very large. It is this equally important that the solvents used are both thermally and chemically stable, giving minimal degradation. Degradation not only reduces the concentration of free amines and the solution absorption capacity, the degradation products can cause environmental problems as well as increase the solution viscosity and foaming tendency and contribute to corrosion.¹ To understand and prevent degradation, identifying the degradation products and the degradation mechanisms of solvents is vital. For the alkanolamines, the degradation with CO₂ has been studied for several compounds, such as MEA²⁻⁴, DEA^{5,6}, DIPA⁷ and MDEA⁸. Lepaumier et al⁹ studied the thermal degradation with CO₂ for several ethanol- and ethylenediamines, identifying main degradation products for the compounds as well as the degradation rates. The thermal degradation of piperazine has also been studied.¹⁰

In this work 28 amines- including alkanolamines, polyamines and cyclic amines - have been tested for thermal degradation with and without CO₂. In addition to determining amine loss, both GC-MS and LC-MS have been used to identify degradation products for the compounds. This forms a very large data set, which consists of both previously tested as well as new compounds, which could be used both to confirm previous studies as well as fill in the gaps.

2. Experimental

The experimental procedure for the degradation experiments has been described in previous work.¹¹ The compound concentrations were determined by Liquid Chromatography-Mass Spectrometry/Mass Spectrometry (LC-MS/MS), using an Ascentis ®Express RP-Amide HPLC Column with a mobile phase consisting of 25 mM formic acid in water. For some of the amines a full scan mode was used in addition to determining the masses of unknown

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compounds. Gas Chromatography-Mass Spectrometry (GC-MS) was used to identify and quantify degradation products. The column used was CPSIL8-CB-Amines, with helium flow and temperature programming optimised for an efficient separation of all the degradation products.

3. Results and discussion

As an example the results for thermal degradation with CO₂ is presented for 4 alkanolamines in table 1, showing the amine loss determined by LC-MS and the main degradation products identified by the GC-MS for these amines. As can be seen from the table, increasing the steric hindrance from ethanolamine (MEA) to 1-amino-2-propanol (MIPA) and 2-amino-2-methyl-1-propanol (AMP) decreases the thermal degradation. However, 2-amino-2-methylpropane-1,3-diol (AMPD) shows higher degradation than AMP. The oxazolidone formation as a suggested first step for the ethanolamines degradation with CO₂⁹ could be plausible, as shown by the degradation products. Similar results will be presented for polyamines and cyclic amines, as well as several other alkanolamines – exploring the impact of chainlength, amine functionality and number of aminogroups among other things. Several of the degradation products have also been quantified, giving an idea of how much of the degradation products which have been detected.

Table 1: Thermal degradation with CO₂ after 5 weeks (* 4 weeks for AMP), and main degradation compounds identified with GC.

Starting amine	CAS	Structure	Amine loss (%)	Main degradation products identified in GC			
MEA	141-43-5		56				
MIPA	78-96-6		19				
AMP	124-68-5		12*				
AMPD	115-69-5		26				

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