

NMR study on the Oxidative degradation of loaded MEA in presence of Fe²⁺

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Introduction

Amine solvents used in CO₂ capture are subject to oxidative degradation due to the presence of oxygen or metal ions in the flue gas. Different techniques have been used to study oxidative degradation of amines in CO₂ capture¹⁻⁵.

Sexton et al. 2009 showed that in the presence of iron catalyst, formate, hydroxyethyl-formamide (HEF), hydroxyethylimidazole (HEI) and ammonia are the major degradation products of MEA oxidation—although 25–50% of degradation products remain unaccounted for. Anionic degradation products were quantified using IC; nonionic degradation products were determined by HPLC and volatile MEA and degradation products were determined by gas-phase FTIR.

In order to identify the volatile organic compounds Strazisar et al. 2003 used combined gas chromatography-mass spectrometry (GC-MS) and combined gas chromatography-Fourier transform infrared absorption spectrophotometry (GC-FTIR). In addition, precise molecular masses of the organic compounds were obtained using low voltage high-resolution mass spectrometry (LVHRMS).

Thermal degradation in presence of CO₂ and O₂ has been studied by Lepaumier et al. 2009 to identify the effects of temperature and gas presence on chemical stability under the experimental conditions. Identification of degradation products was performed with a coupling of gas chromatography-mass spectrometry with EI and chemical ionization (CI). The highest molecular weight compounds were identified with a FT-ICR/MS with electrospray ionization (ESI). In some cases, NMR analyses (¹H and ¹³C) were used to determine compound structure. Formic, glycolic, acetic and oxalic acids, nitrite and nitrate were quantified by ionic chromatography.

Another powerful tool which has been frequently employed to distinguish chemical species in the amine-CO₂-H₂O solutions is Nuclear Magnetic Resonance spectroscopy^{6,7}.

Results and Discussion

In this study we focus on implementing NMR spectroscopy to assign oxidative degradation products of loaded MEA solutions in presence of iron. In order to elucidate the species that might exist in this system, various techniques have been used which include qualitative and quantitative analyses (i.e. 1D and 2D NMR techniques). Using a Bruker Biospin GmbH 600 MHz Ultra shield spectrometer, and 1D (¹H, ¹³C), 2D (COSY; HSQC; HMBC; DEPT 45, 90, 135) experiments, the main degradation products have been identified: N-(2-hydroxyethyl) imidazole (HEI), 2-oxazolidone (OZD), N-(2-hydroxyethyl) formamide (HEF) and N-(2-hydroxyethyl) acetamide (HEA). The quantification of the main degradation products is shown in the figure below.

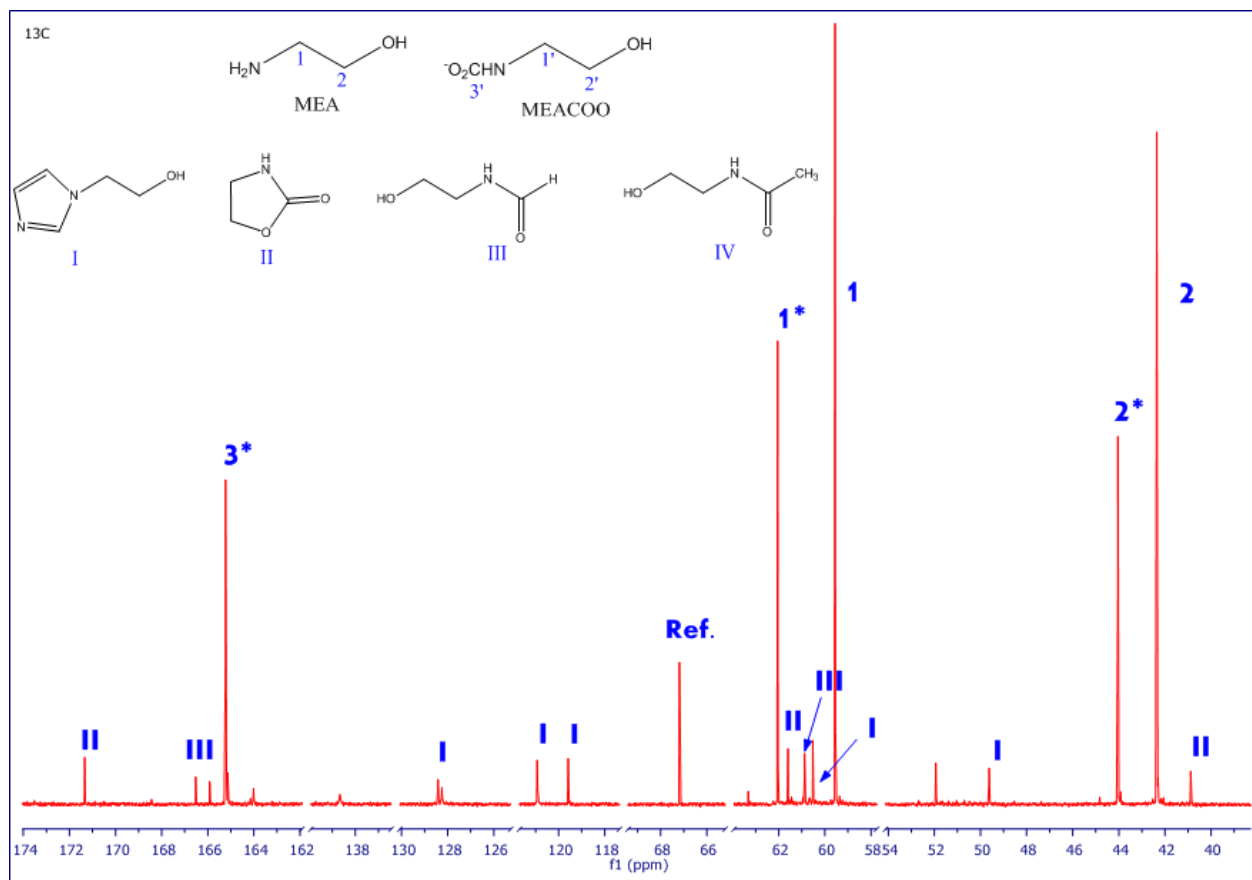


Figure 1. ¹³C-NMR spectrum of degraded MEA in presence of Fe²⁺

Future Work

The main degradation products were identified. However there are still more products not been identified and these will be included in the final work. In addition the quantification of the products an attempt to explain the degradation mechanisms will be reported. A 600 MHz NMR will be employed to magnify the low intensity signal in order to identify the secondary degradation products.

References

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