2-(hydroxyethyl)imidazole: a key marker for MEA oxidation

Rowena E. West,1 Alicia J. Reynolds,1 T. Vincent Verheyen.1

1 Carbon Technology Research Centre, Faculty of Science and Technology, Federation University, Churchill, VIC 3842, Australia

Abstract

The oxidative loss of aqueous amines is a significant operating expense for the post-combustion capture (PCC) of CO2 from fossil fuel-fired power stations. A distinctive UV chromophore present in the MEA oxidation product, 2-(hydroxyethyl)imidazole (HEI), has excellent potential for on-line monitoring the oxidation of alkanolamines such as MEA (monoethanolamine). The characteristic ring structure present in this molecule (and its analogues) is responsible for the UV chromophore. Previous work has readily measured HEI absorbance in degraded alkanolamines from Australian PCC pilot plants. HEI absorbance correlates strongly with the traditional more difficult indicator of amine oxidation, i.e. heat-stable salt (HSS) concentration. This study aims to confirm the theoretical basis for the use of HEI (and its analogues) as indicators of MEA (and other alkanolamine) oxidation.

The synthesis of substituted imidazoles is widely studied as they are a keystone chemical in many pharmaceutical and industrial products. Three reaction mechanisms or systems that are relevant to MEA oxidation under CO2 capture conditions are the Radziszewski synthesis, the Dubus-Bedereck, and hydroxycarbonyl reaction schemes. These three reaction systems share many similarities and readily form HEI (confirmed by HPLC-qTOF) from known MEA degradation products under simple conditions (60°C, 6h, no pH control, 1:1 molar ratios of reactants). One reaction system of particular interest forms HEI rapidly from ammonia, glyoxal, formaldehyde and MEA.

The first step of HEI formation from ammonia, formaldehyde, glyoxal and MEA is the condensation of glyoxal with ammonia and the addition of formaldehyde. A range of compounds are known to form from the condensation of ammonia and glyoxal, including iminoacetaldehyde and ethane-1,2-diimine. Other compounds such as the ethane-2,3-diimine and formaldehyde are also known to form readily. It is likely that formaldehyde was present in the glyoxal solution used in this study because glyoxal is not stable under atmospheric conditions. In the presence of water and ammonia, aldehydes and imines typically exist in equilibrium and may form dimers and oligomers, including the addition product shown in the Figure 1. UV-vis confirmed the formation of these intermediates was almost instantaneous. Although imines and aldehydes are notoriously reactive, we demonstrated that degradation of these precursors did not compromise our calculations as HEI yields did not decrease when the precursors were stored at room temperature for 15 min. Metal-ion mediated oxidation of MEA is likely to produce imines, iminoaldehydes and aldehydes analogous to those formed during the condensation of ammonia and glyoxal.
The rate-limiting step for the synthesis of HEI from ammonia, glyoxal and MEA was determined to be MEA addition to the imine mixture. This reaction was monitored using UV-vis and exhibited a negative activation energy (i.e., the reaction rate was inversely proportional to temperature). A negative activation energy is consistent with the ring formation and suggests that the transition-state or product is in equilibrium with the reactants. This rate-limiting step of HEI synthesis was approximately 0.5-order for MEA, but the reaction-order for the other reagents (ammonia, glyoxal or imines) is elusive due to difficulties establishing the purity and concentrations of glyoxal and other intermediate(s).

The availability of glyoxal, ammonia and imine/aldehyde intermediates, limits HEI formation given that during PCC, MEA is present in significant excess. The limiting of HEI formation by the presence of these MEA oxidation products is consistent with the excellent correlation between HEI concentration and HSS during a pilot-scale PCC campaign in Australia. The mechanism presented in this study predicts that HEI analogues will not form from tertiary amines but will form from secondary (e.g. diethanolamine, DEA) and/or sterically hindered amines (e.g. 2-amino-2-methyl-1-propanol, AMP).

Replacing MEA (a primary amine) with DEA (a secondary amine) lead to a 50% reduction in HEI yield, suggesting that the production of an HEI analogue could be a marker for oxidative degradation of secondary amines. Interestingly HEI is not widely reported as a major product of DEA degradation.

Sterically hindered amines such as AMP are theoretically able to produce HEI analogues with strong UV chromophores because the α-amino carbon does not participate in the ring closure step. While the steric hindrance and the higher basicity of AMP are likely to reduce the rate of HEI-analogue formation, this is not likely to preclude the use these highly UV-active analogues for monitoring purposes. Blended amines used during pilot-scale PCC often include AMP enabling the formation of the HEI analogue (N-(2-amino-2-methyl-1-propanol)imidazole). Investigating the synthesis and UV properties of this AMP product is an important next step for this project.

By determining the mechanism, rate-limiting step and activation energies for the production of HEI during PCC, this research confirms HEI utility as a marker for MEA oxidation. This study has also enabled the prediction of other highly-UV absorbing species that may be useful for on-line monitoring of other oxidation of other amines including AMP. The ability to use straightforward techniques such as UV-vis on-line would be beneficial for the development and operation of PCC technology.