

## FORMATION OF SULFUR AND NITROGEN CROSS-LINKED MACROMOLECULES UNDER AQUEOUS CONDITIONS

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Polysulfides and ammonia are abundant in young depositional environments and play an important role in the formation of macromolecular structures such as protokerogen and humics. In this work we study the co-incorporation of polysulfides and ammonia into simple carbonyl model compounds: octanal and *trans* 2-octenal in order to study their effect on the formation a cross linked macromolecule and suggested a feasible mechanism. The reactions performed in aqueous solutions, ambient temperature and pH~6 to 9 to simulate formation of S and N cross linked polymers in the natural environment. The complex S and N containing polymer studied by <sup>15</sup>N enrichment of the polymer coupled to 2D NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N) techniques and chemical degradation (MeLi/MeI) of the S-S bonds with deuterium labeling followed by GCMS analyses. In addition we apply high-level molecular modeling techniques, Density Functional Theory at the DFT/B3LYP/6-31G\*\* levels and water solvation effects, in order to provide theoretical interpretations and important molecular-level insights on the chemistry. The results shows that polysulfides out compete ammonia in the formation of Michael adducts while ammonia has been shown to compete well at the carbonyl position. The co incorporation of ammonia and polysulfides into carbonyls rapidly form N and S cross-linked polymer. The effect of ammonia and amines on the polymerization processes is via two means: (i) reaction with carbonyls through an imine functionality (Figure 1) and forming oligomers and polymers and (ii) catalysis of the reaction of sulfur nucleophiles on the carbonyl in the formation of *gem*-disulfide/dithiols, enhancing the rate of polymerization. Similar effects are observed when other amines (e.g., glycine) are used instead of ammonia. This catalytic effect achieved by incorporation of sulfur nucleophiles on the intermediate imine, reduces the Gibbs free energy as compared with direct addition to the carbonyl. DFT calculations of several possible transition barriers suggests that this catalytic effect can be also related to proton transfer assisted by the formation of six member rings with ammonia and

*gem* hydroxyl-thiol, resulting in the elimination of water and formation of the very active thioaldehyde. This mechanism is especially important under basic conditions that prevail in most marine environments. These results show that ammonia and amine are intimately involved with sulfur nucleophiles throughout the polymerization processes that occur at low temperatures and are, thus, suggested to be key reactants in the diagenetic formation of protokerogen and humics. This important role of nitrogen is enhances our understanding on the mechanisms at the early preservation stages of organic substances in natural depositional environments.

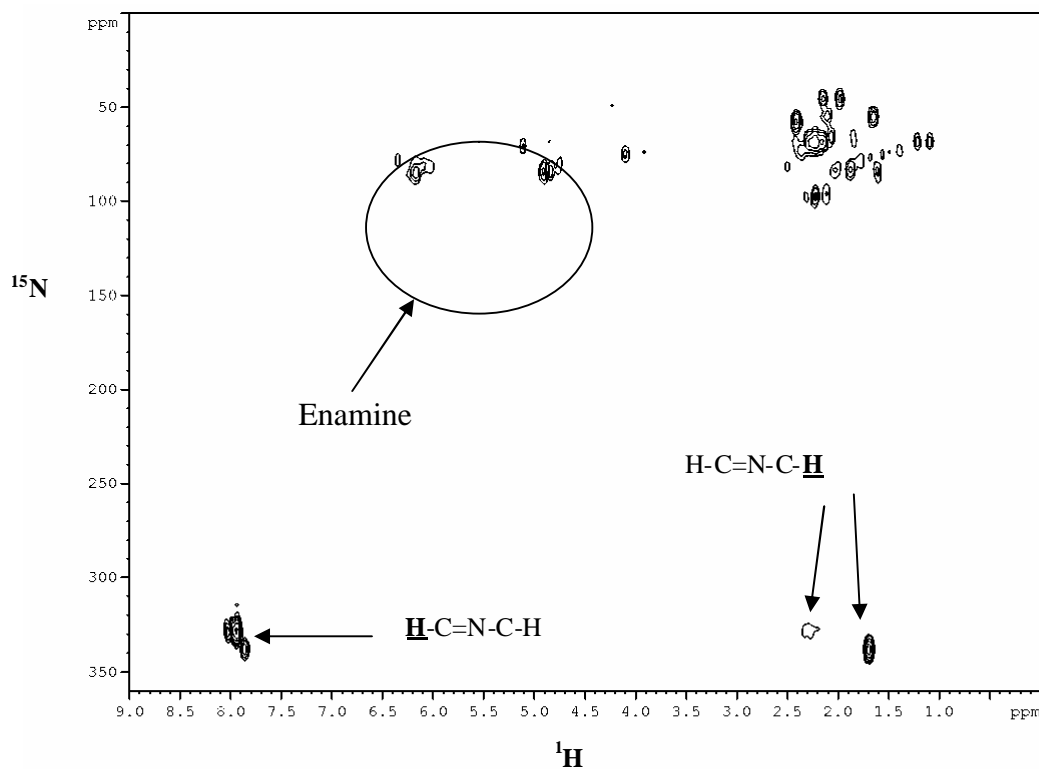


Figure 1. HMBC  $^{15}\text{N}$ - $^1\text{H}$  NMR spectrum for the reaction products between  $(\text{NH}_4)_2\text{S}_x$  and *trans* 2-octenal.