

MOLECULAR MODELING AND EXPERIMENTAL STUDY ON SULFUR ISOTOPES CHANGES DURING SULFUR INCORPORATION INTO ORGANIC MODEL COMPOUNDS

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The reaction between sulfide (or polysulfides) and organic compounds has a significant role in the formation and preservation of sedimentary organic matter (SOM). Although the mechanisms for the formation of the sulfurized products were studied, not enough attention was given to the stable isotope ratio $^{34}\text{S}/^{32}\text{S}$ ($\delta^{34}\text{S}$) changes in these reactions.

The isotope fractionation during the reaction of inorganic reduced sulfur species and organic model compounds has recently been investigated (Amrani and Aizenshtat 2004). This study shows that the reaction of polysulfide anions with carbonyl compounds has a ^{34}S enrichment of 4-5‰ at equilibrium. However, this study used polysulfides anions as nucleophiles assuming that the very complex polysulfide solution is isotopically homogenous and there is no ^{34}S enrichment of the polysulfide as compare with the sulfide species in the same solution. A recent study challenged this idea showing that polysulfides are indeed ^{34}S enriched by up to 6‰ as compare with the sulfide anions (Amrani et al., 2006). These finding may suggest that the observed ^{34}S enrichment of the organic sulfur compounds is not due to ^{34}S enrichment during the addition of sulfur into organic matter but rather selective addition of polysulfide anions into the aldehydes. This assumption is supported by the extremely higher reactivity of polysulfide in comparison with sulfide anions ((Loch et al., 2002).

In the present study, we combined theoretical calculations with experimental work in order to distinguish between these two mechanisms. We reacted aldehydes and haloalkanes with aqueous solutions of CH_3SNa or HS^- at pH=8-9 at 25°C. The reaction with CH_3SNa can not form polysulfides and therefore the isotopic effect can be attributed to the formation of C-S bond and measure its $\delta^{34}\text{S}$ without the bias of polysulfide fractionation. The reaction with H_2S took place in an oxygen free environment to prevent oxidation of H_2S and formation of polysulfides. The results showed clearly that the incorporation of CH_3SNa results in ^{34}S enrichment between 3.0 to 5.3‰. The main products from the reaction with the aldehydes were *gem* di-sulfides. The isotopic results are in a good agreement with thermodynamic calculations that put the upper limit for this enrichment at 5.5‰ for aldehydes. The reaction

with H₂S (actually HS⁻) yielded the same general products but the isotopic enrichment was higher 5.5-7.8‰. Molecular modeling for this reaction put the upper limit for this isotopic enrichment at 9.3‰ for aldehydes. These results demonstrate an equilibrium isotope effect (Figure 1) as the reaction of aldehydes with sulfides is known to be reversible. Reaction with haloalkanes can demonstrate different mechanism controlled by kinetic isotope effect, as the results ranges between -3‰ to 0‰. Molecular modeling for these reactions involves the location of a transition state with high-level Density Functional Theory (DFT) calculation at the DFT/B3LYP/6-31G** levels and are still in progress. Currently we study the isotope effect of other functionalities (such as conjugated double bonds etc.) in the incorporation of H₂S under an anaerobic environment, from both molecular modeling and experimental approaches. In addition to the bulk measurement, organo-sulfur products will be isolated to individual compounds and measure for their δ³⁴S value to give a better understanding of the mechanism pathway. The results of this study will help to interpret the isotopic differences that are often observed between OS and pyrite and may give insight into sedimentary organic sulfur composition and mechanism of formation as connected to their δ³⁴S measured values.

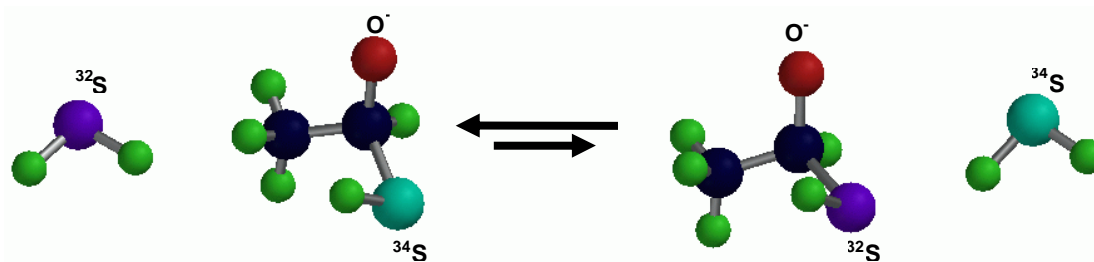


Figure 1. Isotopic equilibrium between ³²S and ³⁴S during reaction of H₂S with aldehyde.

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