Experimental investigation on one of the potential generation mechanisms of dibenzothiophene (DBT) and its methylated homologues

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Dibenzothiophene (DBT) and its methylated homologues (DBTs) are one kind important polycyclic aromatic sulfur heterocycles (PASHs) in petroleum and sedimentary organic matters. Although the geochemical parameters with DBTs have been widely applied in petroleum prospecting, such as sedimentary environment evaluation of oils and related source rocks, maturity assessment, oil-source correlation, and oil migration tracing, their potential occurrence mechanisms is still an open question.

In this study, we conducted the thermal simulation experiments in anhydrous close systems in gold tubes. The starting materials are 3,3'-dimethylbiphenyl (3,3'-DMBP) and element sulfur. The experimental temperatures were 200 ℃, 300 ℃, 400 ℃ and 500 ℃, respectively, while the experimental pressure was constant at 10 MPa. Each experiment lasted for 24 hours. After cooling the tubes, we pierced the gold tube with a needle. The lead acetate paper turned to black when it contacted the gaseous product. It indicates that the presence of H_2S after the experiments. The opened gold capsules, along with a few pieces of copper sheets, were kept in CH_2Cl_2 for 12 hours, in order to exclude unreacted element sulfur. The CH_2Cl_2 solution of the products were then filtered with absorbent cotton, which were exacted with CH_2Cl_2 for 24 hours. The prepared sample solution was analyzed using gas chromatograph – mass spectrograph.

The identified products from GC-MS demonstrates several new points:

(1) Temperature constrains the product species and the relative abundances. Biphenyl (BP) and DBT, and their corresponding homologues, are stable in different temperature regions. For example, with the increasing temperature, the relative abundance of 4-, 3-/2-, and 1-MDBT in our experimental product changes. At 200 ºC, only 1-MDBT is present. Trace 4- and 3-/2-MDBT are detected from the 300 ºC-experiment. The ratio of 4-MDBT/1-MDBT is approximately 9:1 at 400 ºC. This trend of this elevated ratio is consistent with the observation from the investigations on the maturity of oil with MDBTs concentrations. However, the ratio of 4-MDBT/1-MDBT decreases to 2:1 at 500 ºC. It indicates that the use of this index for oil maturity could be suffered temperature upper limit.

(2) DBTs, initialing with 3,3'-DMBP and sulfur, can be produced down to 200 ºC. This is much lower than 300 ºC reported in previous studies(Asif et al., 2009; Xia and Zhang, 2002). It highly increases the possibility that this reaction could be one potential mechanism for the DBTs occurrence in sedimentary basins.

(3) Only three DMDBTs (4,6-, 2,6-, and 2,8-DMDBT) are detected in 300 ºC and 400 ºC experiments, but no obvious DMDBT are produced under 200 ºC or 500 ºC. It verifies the mechanism of these DMDBTs generation in the sedimentary basins, which was proposed by

Li et al. (2013) on the basis of chemical reaction pathway (Figure 1). It should be also noted that this mechanism is reasonable under suitable temperatures. DMDBTs will be decomposed when temperature is too high.

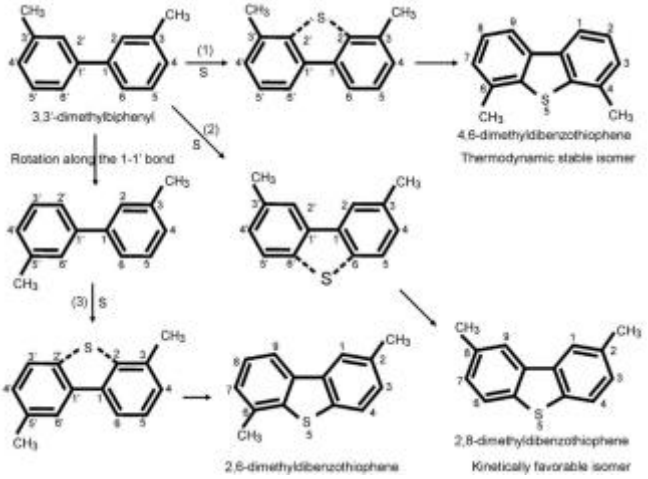

Figure 1 *Proposed scheme of reaction pathways of 3,3'-DMBP to 4,6-DMDBT, 2,8-DMDBT and 2,6-DMDBT (cited from Li et al., 2013)*

References:

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