Petroleum Geology & Experiment No. 02

Citation: WU Jia, QI Wen, LUO Qingyong, CHEN Quan, SHI Shengbao, LI Meijun, ZHONG Ningning. Experiments on the generation of dimethyldibenzothiophene and its geochemical implications [J], Petroleum Geology & Experiment, 2019 (02): 260–267.

Experiments on the generation of dimethyldibenzothiophene and its geochemical implications

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Abstract: Dibenzothiophene (DBT) and its homologues are important molecular markers in petroleum geochemistry. However, DBT-related geochemical indicators were derived mainly based on empirical observations due to insufficient understanding of the mechanisms through which these organosulfur compounds were generated in sedimentary environment. Thermal simulation experiments with 3,3'-dimethylbiphenyl (DMBP) and sulfur in closed gold tubes at 200 ℃–500 ℃ and 10 MPa afforded three main dimethyldibenzothiophene isomers (DMDBTs). Importantly, DBTs could be generated at a temperature as moderate as 200 ℃ under geological conditions, because the temperature threshold of the reaction could be reduced by increasing the system pressure. Further investigations revealed that the regioselectivity of the thiophene formation reaction was strongly influenced by temperature. This is similar to the process that occurs in natural geological systems. It should also be noted that the maturity index 4-/1-MDBT (MDR) reaches a maximum around 1.5% (Easy%R_o). It indicates that MDR index should be used in a suitable maturity regions combined with the given geological setting.

Keywords: dibenzothiophene; generation mechanism; thermal simulation; maturity

Dibenzothiophene compunds (DBTs) are the important compounds of sulfur-containing heterocyclic aromatic hydrocarbons in crude oil and sedimentary organic matters, exhibiting good thermal stability [1]. Since the mid-1980s, geochemists have successively detected and identified DBT and its C_1- to C_3- substituents in aromatic hydrocarbon components of crude oil [2–4] and the related geochemical parameters have been widely applied to indicate the sedimentary environment of source rocks [2,5–7], judge the maturity of crude oil [8–12], track the migration direction of oil and gas, and compare the oil sources [13–16]. However, there are also a certain limitations in the practical applications of DBTs series parameters. For example, when the “trifluorene” indicator is utilized to determine the sedimentary environment of source rocks or crude oil, if the methyl-substituted homologues of “trifluorene” series are included in the statistics, the ratio of dibenzofuran (DBF) to DBT will be increased, thereby affecting the judgment results of this indicator [17]. For the transitional sedimentary environment, the distribution of “trifluorene” compounds in the plate is too scattered to accurately indicate the sedimentary environment [18]. Therefore, clarifying the geochemical genesis of DBTs is critical to understanding the applicability and limitations of this indicator.

In recent years, there have been many controversies about the geochemical formation mechanism of DBTs. Since the sulfur content in petroleum is much higher than that of the biological organism itself, and the occurrence state of sulfur element is significantly different in the two. Hence, in the immature and low maturity stages, the lipid compounds can be combined with the reduced sulfur (S or H_2S) to form complex and diverse thiophene compounds [19–20]. WHITE et al., [21] proposed that the thiophene organosulfides could be formed by the reaction of aromatic hydrocarbons with elemental sulfur when studying the aromatic compounds in coal. XIA et al. [22] and ASIF et al. [23] found that biphenyl compounds (BPs) were potential DBTs precursors through thermal simulation experiments. The abundance of 3,3'-dimethylbiphenyl (3,3'-DMBP) in the source rocks of the Liaohe Basin shows good positive correlation with the total sum of that of three corresponding dimethyldibenzothiophenes (4,6-, 2,6- and 2,8-DMDBT), indicating that DMBPs

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Received: 2018-08-17

Supported by: National Key R&D Program “Evaluation on The Oil and Gas Generation in Ultra-deep Environment and The Effectiveness of Hydrocarbon Kitchen” (2017YFC0603102); National Natural Science Foundation of China (41403049); Independent Program of National Key Laboratory of Oil and Gas Resources and Exploration (PRP/indep-3-1715)

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may be the precursors of some DMDBTs [24]. However, the above understandings are mainly based on the speculation of the chemical reaction principle and the comparison of geological samples, and there is still lack of the direct evidence of laboratory simulation. In order to verify the relationship between alkylbiphenyl and alkyldibenzothiophene, and better understand the geochemical behavior of DBTs formation mechanism, this paper took 3,3'-DMBP and elemental sulfur as research objects, and applied the closed system thermal simulation experiment so as to study the geochemical characteristics of DBTs formation under sedimentary basin conditions, namely the threshold temperature, formation mechanism and thermal evolution behavior of DBTs generation. The results of this study can be helpful in better understanding and applying the geochemical parameters related to DBTs.

1 Experiment

1.1 Experimental samples and reagents

The experimental samples included 3,3'-DMBP ($C_{14}H_{14}$, molecular weight of 182, purity of larger than 98%, Tokyo Chemical Industry, Tokyo), sulfur powder (purity of 99.5%, 325 mesh, Alfa Aesar), 4-methylbiphenyl (4-MBP, $C_{13}H_{12}$, molecular weight of 168, purity of 98%, Alfa Aesar), biphenyl (BP, $C_{12}H_{10}$, molecular weight of 154, purity of 99%, Acros Organics). The solvent used in this experiment was the re-distilled dichloromethane (CH_2Cl_2, purity of larger than 99%). The 0.608 g of sulfur powder and 0.616 g of 3,3'-DMBP were taken separately in a 5 mL beaker, stirred with a glass rod for 15 min, mixed thoroughly, and sealed and stored as the reactants of thermal simulation experiment.

1.2 Thermal simulation experiment

The thermal simulation experiment of the closed system gold tube was carried out in the Hydrogen Generation Kinetics Laboratory of the State Key Laboratory of Oil and Gas Resources and Exploration, and the ST-120-II gold tube thermal simulation experimental device was utilized. The gold tube (length of 30 mm, inner diameter of 5.5 mm and wall thickness of 0.25 mm) was fired for 3 min with a butane-air flame at approximately 800 ℃. After the cooling process, one end of this tube was welded with a micro argon arc welding machine (PUKU4, Lampert Werktechnik GmbH). About 50 mg of the sample was taken and placed on the bottom of gold tube. Before being sealed, argon was continuously purged into the tube for 3–5 min; then, the open end of gold tube was squeezed tightly, sealed with an argon arc welding machine, and the total mass after welding was weighed. Two parallel samples should be set for each temperature point. The sealed gold tube was placed into the corresponding cauldron, and was heated from room temperature to 125 ℃ in 10 min. Hold it for 5 min, then raise it to the target temperature at 10 ℃/min, keep the temperature constant for 24 h, stop heating, and cool it naturally to room temperature. The experimental pressure was 10 MPa, and the experimental temperatures were 200, 300, 400, and 500 ℃, respectively. After the end of the experiment, the gold tube was taken out for weighing, and the total masses of the gold tube before and after the experiment were compared to judge the sealing property (Table 1).

Table 1 Quantities of samples and total masses of gold tubes before and after annealing

Sample number	Sample mass/g	Total mass after welding/g	Total mass after experiment/g
200′-1	0.028 (3,3′-DMBP) + 0.026 (S)	2.976	2.974
200′-2	0.042 (3,3′-DMBP) + 0.043 (S)	2.721	2.725
200-1	0.051	3.000	2.999
200-2	0.053	2.914	2.914
300-1	0.051	3.034	3.035
300-2	0.050	3.136	3.136
400-1	0.053	2.885	2.885
400-2	0.048	2.728	2.729
500-1	0.052	3.192	3.193
500-2	0.051	3.023	3.031

1.3 Post-processing of experimental products

After the end of the thermal simulation experiment, the products in the closed system shall be separated and recycled. The post-processing was conducted in the Asphalt Chemistry Laboratory of the State Key Laboratory of Oil and Gas Resources and Exploration of China, and the specific steps are as follows:

(1) Clean the surface of gold tube with methylene chloride and allow it to be completely volatilized.

(2) Place the gold tube in a closed pipeline and vacuumize it to a vacuum condition with an internal pressure of 5 kPa.

(3) Puncture the gold tube, release the gas inside the tube, wait for 0.5 min to make the gas inside the pipeline spread evenly, and extract partial gas sample from it with a syringe.

(4) Use a wet lead acetate test paper to detect whether the gas product contains H_2S.

(5) Take out the gold tube from the pipeline, cut it off and expose the inner surface thoroughly, and then place the gold tube into a clean glass bottle. Immerse it fully into dichloromethane solvent, and shake it for 15 min to dissolve the residual organic matters on the tube fully.

(6) Add three to five pieces of clean copper to the glass bottle and let it stand for 24 h to remove residual elemental sulfur.

(7) Filter and elute all the contents of the glass bottle, collect all the filtrate in the sample bottle, and seal and store it for chromatographic–mass spectrometry.

1.4 Qualitative analysis of liquid products

Qualitative analysis of the chemical composition of the experimental products was performed in the Biomarker Laboratory of the State Key Laboratory of Oil and Gas Resources and Exploration of China. The test instrument was an Agilent 6890 GC-5975i MS GC/MS equipped with HP-5MS (5% phenylmethylpolysiloxane) elastomeric quartz capillary column (60 m × 250 μm × 0.25 μm). The chromatographic analysis was conducted with the programmed temperature rising at the initial temperature of 80 ℃, holding the temperature for 1 min, and raising it to 260 ℃ at a rate of 3 ℃/min; the carrier gas was helium, the flow rate was 1 mL/min, and the average column flow rate was 26 cm/s; the sample was injected with splitless injection and the inlet temperature was maintained at 300 ℃. In the mass spectrometry, the ion source was electron impact (EI), the power voltage was 70 eV, the mass spectrum scanning range was *m*/*z* = 50–450, and the data were acquired by full scan (SCAN) + selective ion (SIM) simultaneously.

In this study, the main chemical components of the products were qualitatively identified by standard co-injection and retention time index [25–26]. Shi et al. [27] studied the C_1- and C_2-DBT in petroleum and sedimentary organic matters. The mass-to-charge ratios of ion fragments selected in the GC-MS test were *m*/*z* 154 (BP), *m*/*z* 168 (MBPs), *m*/*z* 182 (DMBPs), *m*/*z* 184 (DBT) *m*/*z* 198 (MDBTs), and *m*/*z* 212 (DMDBTs).

2 Results and discussion

2.1 Qualitative identification of experimental products

The gas product presents a pungent odor like rotten egg, and makes the wet lead acetate test paper gradually turn white from black, indicating that this product contains H_2S. The main products of the soluble organic matters in the reaction system can be identified by GC-MS (Fig. 1). Since the dilution factors used during the post-processing are different, the peak area in the spectrum cannot be used for lateral comparison of the absolute concentrations of the products. The identification of DBTs (DBT, 4-MDBT, 3-/2-MDBT, 1-MDBT, 4,6-DMDBT, 2,6-DMDBT, 2,8-DMDBT, etc.) was based on the retention time (RT) of naphthalene and phenanthrene, determined by comparing their literature values with their retention indices [27]. The BP series of compounds were identified by adopting the standard compounds as external standards.

According to the differences on reactants and products, the newly formed major products (BP, 3-MBP, DBT, MDBTs, and DMDBTs) can be identified (Fig. 1). Among them, the peak of 3,3'-DMBP in all the spectrums is very obvious (RT of 34–35 min). In the TIC spectrum of the reactant 3,3'-DMBP, there are also undetermined peaks of 3-MBP, 4-MBP (RT 30–31 min) and five kinds of impurities (RT of 37–42 min). BP, DBT, MDBTs and DMDBTs are not detected in the reactants. MDBTs and DMDBTs are detected in the experimental products, but the concentrations are low in the experiments at 200 ℃ and 500 ℃. The peak area of DBT shows an opposite characteristic to that of MDBTs. The peak area of DBT is more prominent than that of MDBTs in experiments at 200 ℃ and 500 ℃, but weak in experiments at 300 ℃ and 400 ℃. 3-MBP and 4-MBP are always present in the products, but the relative concentrations are varied, reflecting the demethylation of 3,3'-DMBP to some extent. At 500 ℃, the presence of a large number of BPs indicates the strong demethylation of MBPs and DMBPS at high temperatures.

2.2 The formation temperature of DBT and its homologues

Xia et al. [22] and ASIF et al. [23] studied the processes of BP and MBPs reacting with sulfur to form DBT and MDBTs, respectively. It was found that 3,3'-DMBP and elemental sulfur could react and form DBT, MDBTs and DMDBTs (Fig. 1), indicating that the reaction is thermodynamically feasible at 200 ℃ and 10 MPa. It is worth noting that ASIF et al. [23] did not detect DBT (MDBTs) in the 200 ℃ catalyst-free experimental product, but DBT (MDBTs) were detected in the products of comparative experiment that took activated carbon or sub-bituminous coal as the catalysts. However, in this study, a huge amount of DBTs were formed in the catalyst-free, 200 ℃ experiment. This difference is most likely due to different pressures, and the mechanism can be explained in two aspects: (1) higher pressure (10 MPa) will promote the occurrence of chemical reactions, so high pressure will reduce the activation energy required for the chemical reaction between BPs and sulfur; (2) both BPs and sulfur are volatile substances that can fill the reaction vessel in a gaseous form at high temperature. High pressure will increase the fugacity of gaseous reactants and accelerate the reaction, and such effect is more remarkable than that by using activated carbon to increase the contact area of reactants.

Under general geological conditions, the hydrostatic depth corresponding to 10 MPa is about 1 000 m, indicating that the reaction of DMBPs and sulfur forming DBTs can occur in shallow formations. RADKE et al. [28] found that the abundance of DBTs was very low (10–15 μg/g) in immature core samples (R_o = 0.44%−0.48%). After entering the “oil window”, their content increased rapidly, and the R_o of Kimmeridge mudstone increased from 0.45% to 0.65%, and the DBT content increased from 2.1 μg/g to 43.0 μg/g accordingly. Similar cases have been reported in the studies of SCHOU et al. [29] and LI et al. [30]. Although the above studies suggest that the massive generation of DBTs can only occur after the organic matters enter the “oil window”, the fact cannot be ignored that the organic matters have already produced DBTs when they are immature. In this study, the

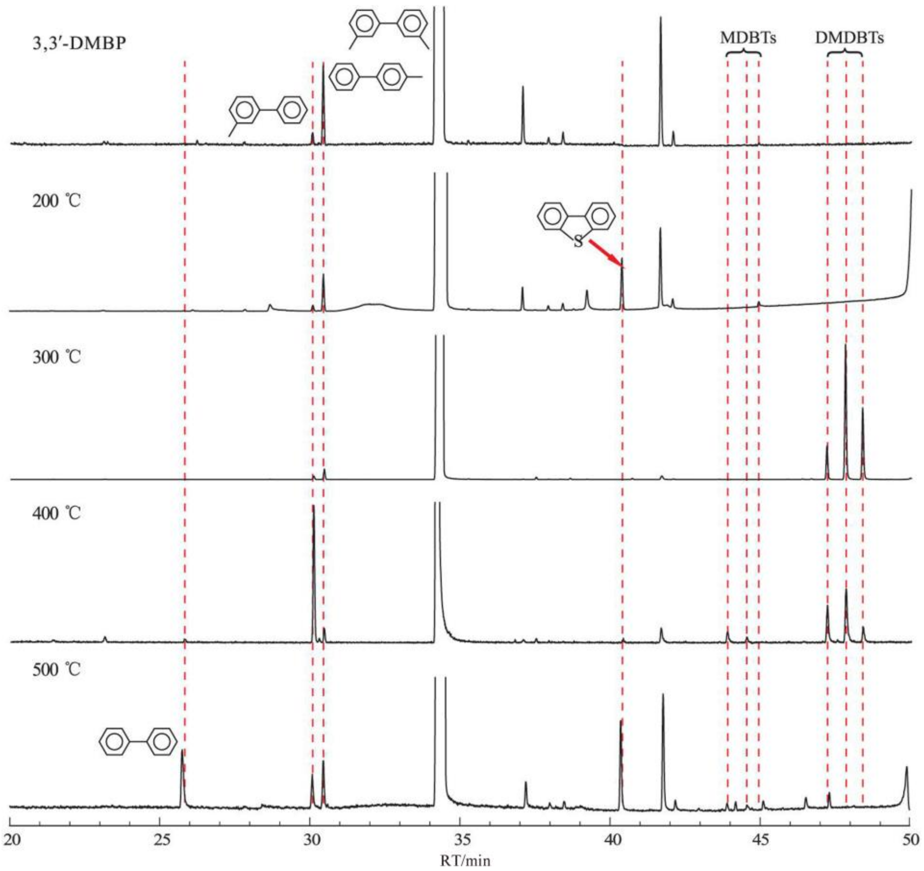
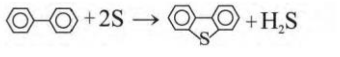


Fig. 1 Total ions chromatograms of the reactant 3,3′-DMBP and the main experiment products at 200 ℃–500 ℃

equivalent vitrinite reflectance (Easy%R_o) corresponding to the 200 ℃ experiment is 0.30% [31]. DBTs are detected in such low maturity experimental products (Fig. 1, 2), identifying the consistency of the experimental results with geological observation. Considering that various common minerals and organic polymers in the formation will catalyze the hydrocarbon reactions [32–36], the reaction temperature threshold for generating DBTs through the reaction between BPs with sulfur should be less than 200 ℃.

2.3 Potential formation mechanism of DBT and its homologues

The process of generating DBTs by BPs and S is a chemical reaction. Taking BP as an example, the basic reaction formula is as follows:



(1)

From the perspective of mass conservation, a sulfur atom can form a new thiophene ring with two adjacent benzene rings on BP, and the substituted H atom can combine with other sulfur atoms to form H_2S. In the course of reaction, the compounding reaction inevitably undergoes the process of S atom attacking No. 2 carbon of BP molecule, which forms two C-S bonds to form a thiophene ring. After the ring is formed, due to its rigid structure, the possibility of conformational isomerization will be lost. Therefore, if BP has a substituent on No. 3 carbon, at least two isomers will appear in the reaction products; if there is a substituent on No. 2 carbon, the type of experimental products will be limited due to the steric hindrance.

In this study, only three kinds of DMDBTs (4,6-, 2,6- and 2,8-DMDBT) are detected in the experimental products at 200 ℃–400 ℃, and the relative content of 2,6-DMDBT is always the highest (Fig. 2). The 3,3'-DMBP molecule has two stable conformers (Fig. 3, A and B). The steric hindrance of the 3,3'-DMBP conformation B is smaller than that of the conformation A. The thermal stability and the presence ratio of the former are high, and the sulfur atom has a greater probability of attacking the stereoisomer of conformation B, so the corresponding product 2,6-DMDBT will have the highest relative content. In the other two products, the two intramolecular hydrogen bonds of 4,6-DMDBT make its thermodynamic stability better than that of 2,8-DMDBT, so when the system is dominated by thermodynamic factors, the content of 4,6-DMDBT is higher than that of 2,8-DMDBT. However, in the path of forming 2,8-DMDBT, the steric hindrance of the S attacking 3,3'-DMBP is much smaller than that of the path forming 4,6-DMDBT (Fig. 3). In the appropriate interval, the temperature rising will lead to the higher formation rate of 2,8-DMDBT rather than 4,6-DMDBT, so the kinetic-dominated reaction results in the reversal of their area ratio at 300 ℃. When the temperature continues to rise, the peak area of DBT gradually becomes obvious, indicating that the decomposition rate of DMDBTs is increased, and the formation of DMDBTs changes back to thermodynamic factors dominant.

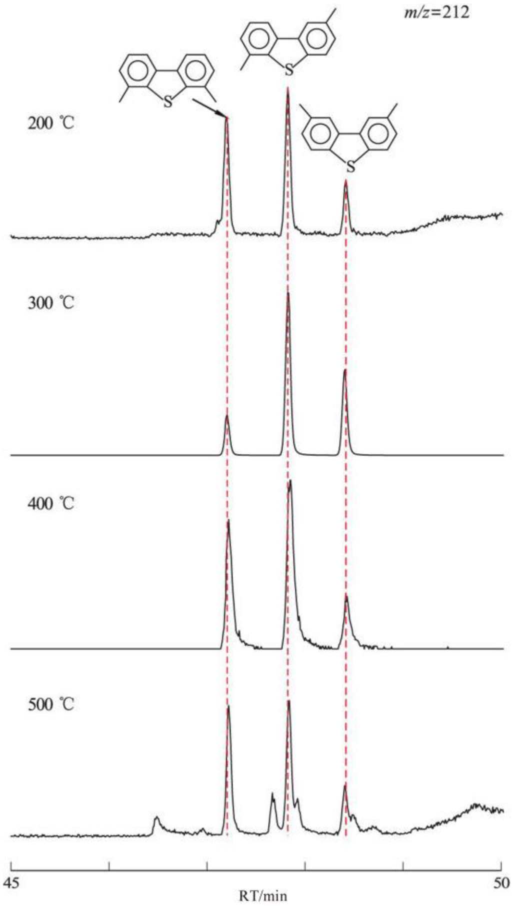


Fig. 2 Mass chromatograms of DMDBTs in experiment products (*m*/*z* 212)

The distribution patterns of three DMDBTs in the experiment are not the same as those in the geological samples, but the trends are in line with the basic thermodynamic laws. In this study, the Easy%R_o values corresponding to the 200 ℃ and 300 ℃ experiments are 0.30% and 0.64%, respectively. Among the experimental products corresponding to both of them, the highest relative abundance is 2,6-DMDBT in both experiments, the 4,6-/2,8-DMDBT ratio is higher than 1 in the 200 ℃ experiment, and is lower than 1 in the 300 ℃ experiment (Fig. 2). LI et al., [30] studied the geological samples of the Liaohe Basin, and found that from the immature stage to the mature stage (R_o = 0.32%–0.73%), the 4,6-DMDBT has the highest abundance, and its relative contents in the 4,6-, 2,6- and 2,8-DMDBT continue to increase. Since 2,8-DMDBT exhibits the lowest thermal stability among the three, its relative content is low and decreases with maturity. Therefore, in this study, the phenomenon that the ratio of 4,6-/2,8-DMDBT increases with maturity is consistent with the actual geological observation [24].

It is worth noting that the distribution of those three DMDBTs isomers under actual geological conditions is mainly controlled by thermodynamics. In this study, the distribution of the experimental product at 300 ℃ highlights the kinetic control factors, which may be due to the high purity of the reactants. In the actual formation, the concentrations of these molecular markers are relatively low, the relevant reaction rate is limited by concentration, and the reaction rate is very low, so the distribution of products is more subject to the thermodynamic influence. In addition, the types of DMDBTs isomers in the actual formation are not only limited to the above three. The relationship between other isomers and 4,6-DMDBT is unclear, and the catalytic or intermolecular interactions of inorganic minerals or sedimentary organic matters in the formation may affect the conformational distribution of the reactants and the distribution state of DMDBTs product.

Except for the reactant 3,3'-DMBP, no other isomers of DMBP are detected in the products. The correspondence between the reactants and the products of 3,3'-DMBP and 4,6-, 2,6-, 2,8-DMDBT can be confirmed on the premise that the configurations of both the reactants and products are limited. This result is consistent with the viewpoint of ASIF et al. [23], and also confirms LI's early hypothesis about the relationship between the precursors and products while studying DMBPs and DMDBTs in the sedimentary organic matters of the Liaohe Basin (Fig. 3) [24]. It is worth noting that there are three additional small peaks in the product TIC at 500 ℃, but there is no new peak signal near the DMBP. These three peaks are largely the isomers produced by the methyl migration of three existing DMDBTs, indicating that the activation energy required for methyl migration reaction is too high, may occur only under specific geological conditions.

2.4 Effect of temperature on thermal maturity parameter MDR

The ratios of MDBT isomers are significantly different at different temperatures (Fig. 4). At 200 ℃–300 ℃, the abundance of 1-MDBT is significantly higher than that of other isomers. At 400 ℃, the relative abundance of 4-MDBT is dominant. At 500 ℃, although the abundance of several MDBTs is different, the difference is less pronounced than that at low temperature. Since there are only traces of MBPs in the initial reactants of this study, the MDBTs should be formed by demethylation during thermal simulation experiments. At the same time, when the temperature is lower than 300 ℃, the effect of temperature rising on 4-/1-MDBT (MDR) is weak, increasing only from 0.01 to 0.04. From 300 ℃ to 400 ℃, the MDR is increased rapidly to 9.4, and after 400 ℃, the MDR trend is reversed, dropping to 1.07 at 500 ℃ (Fig. 5).

Since 4-MDBT has intramolecular hydrogen bonds, its thermal stability is higher than that of 1-MDBT. As the thermal evolution deepens, the relative content of 4-MDBT

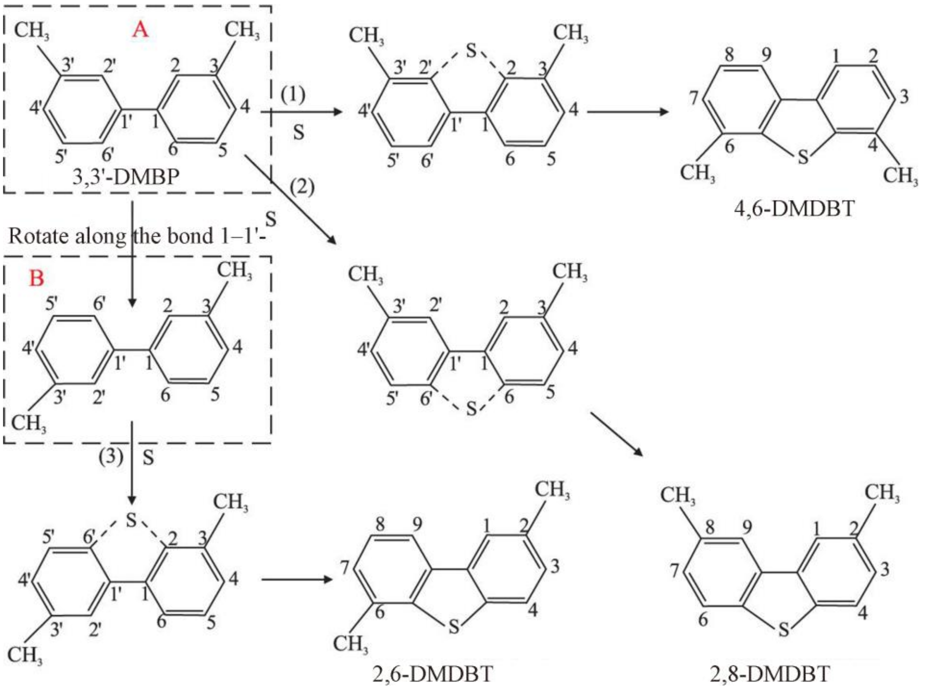


Fig. 3 Reaction pathway of 4,6-, 2,8- and 2,6-DMDBT generated from 3,3’-DMBP [24].In the virtual boxes, A and B represent the two stereocosmic conformations of 3,3'-DMBP.

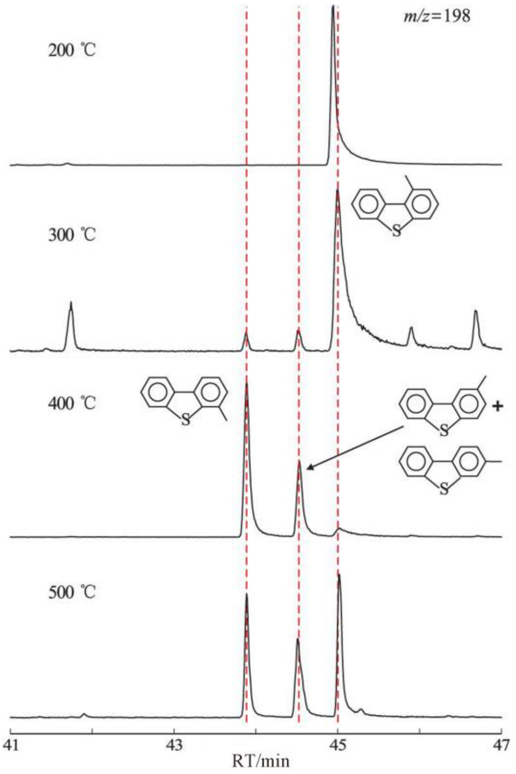


Fig. 4 Mass chromatograms of DMDBTs in experiment products (*m*/*z* 198)

increases gradually, so MDR increases monotonically with maturity [3,37]. RADKE analyzed the rock samples from different strata in different regions (the Lower Cretaceous Wealden, Posidonia, Kim-Meridge shale, the Cretaceous shale Lias Series α and δ groups, and the Dogger Series β and γ groups), and found that when the average vitrinite reflectance was 0.4%–1.2%, there was good positive correlation between MDR and R_o (the correlation coefficient reached 0.84) [38]. However, in this study, MDR shows an extreme value at around 400 ℃ (Easy%R_o = 1.49%, mature stage), and then it is reversed. Both DBT and phenanthrene are tricyclic aromatic hydrocarbons that should have similar thermodynamic behaviors. The maturity parameter methylphenanthrene index presents the same periodic reversal, so this geochemical behavior of MDR is understandable.

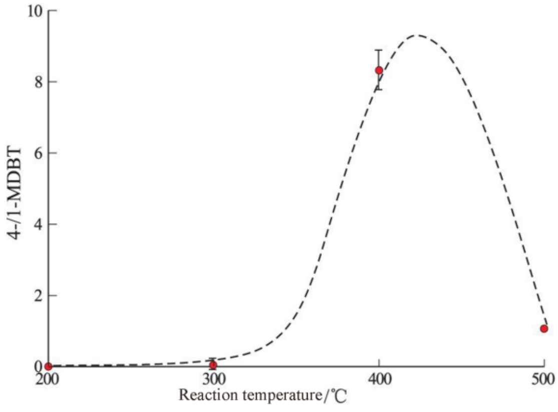


Fig. 5 Relationship between MDR (4-/1-MDBT) and temperature

This phenomenon has been reported in many geological cases. BAO et al. [5] found that the maximum value of MDR appeared in the buried depth of 1 950 m (R_o = 1.2%) when studying the exploratory well profile of the Huangqiao area in the Lower Yangtze Basin. When studying the core samples of the Ruhr coal basin, RADKE [39] found that the maximum value of MDR was corresponding to the R_o of 1.58%. Although the trend of MDR has been recognized, its application is largely restricted. SCHOU et al. [29] found that the monotonically increasing interval of MDR was from immature (T_{max} = 420 °C) to the "oil window" (T_{max} = 446 ℃). Li et al. [40] reported that the MDR monotonically increased with maturity in the interval of 0.7%–1.35%. This interval is in alignment with the temperature range of 300 ℃–400 ℃ (Easy%R_o = 0.73%–1.49%) in this study. Below 300 ℃ or above 400 ℃, the trend of MDR changes abruptly. Since the MDR parameters are susceptible to the sedimentary environment, lithology and organic matter types, at present there is no MDR-based universal empirical formula for maturity. Therefore, it is necessary to pay attention to the application scope when we use MDR to judge the super/over-mature crude oil or the maturity of sedimentary organic matters.

3 Conclusions

(1) During the thermal evolution of sedimentary organic matters, 3,3'-DMBP and elemental sulfur can interact to form DBT and its homologues. Increasing the pressure is able to lower the reaction threshold temperature, which may be below 200 ℃ under the geological conditions.

(2) In the experiment, the products 4,6-, 2,6- and 2,8-DMDBT can be generated according to the spatial configurations. Under the geological conditions, the concentration distributions of the above three DMDBTs are thermodynamically dominated, and the results of this experiment clearly reflect the influence of kinetic factors, largely because the concentration of the reactants is too high, resulting in the apparent chemical behavior variation of the reaction.

(3) In the thermal simulation experiment, the products are affected by the kinetic factors proportionally. Although the different geological conditions lead to the different distributions of the above three DMDBTs, the previously proposed reaction generation path is still verified.

Acknowledgements

Acknowledgement: This article has received technical supports from Gao Shuo, graphic editing assistance from Jin Xiao, and the constructive comments from editors and anonymous reviewers, special thanks to all the helps!

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