The role of sulfur in the pyrolysis of kerogen

QIN Yan¹,², PENG Ping’an¹, YU Chiling¹ & LIU Jinzhong¹

1. State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China;
2. Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

Correspondence should be addressed to Peng Ping’an (e-mail: pinganp@gig.ac.cn)

Abstract Sulfur plays an important role in the generation and evolution of hydrocarbon from organic matter. Here, a pyrolysis experiment in closed system was performed on Maoming oil shales kerogen (Type I), Maoming oil shales kerogen added with sulfur ether and Maoming oil shales kerogen added with sulphur. The results suggest that the existence of sulfur can result in: (i) higher yield of hydrocarbons generated from the kerogen; (ii) decrease of the temperature for the maximum generation of heavy hydrocarbons (the C₁₅₊ fraction) by 20°C; (iii) decrease of the temperature for the maximum generation of the aromatics fraction by 40°C, and (iv) acceleration of the aromatization process. The pyrolysates from kerogen added with sulfur are similar to the heating products of the sulfur-rich kerogen as reported in the literatures. It seems that the sulfur catalysis is also an important factor that can make the sulfur-rich kerogen generate low-mature oil at the earlier diagenesis stage, except for the weakness of the C-S and S-S bonds.

Keywords: kerogen, hydrocarbon generation, thermal simulation, sulfur catalysis, Maoming oil shale.

DOI: 10.1360/04wd0342

Sulfur plays an important role in the process of hydrocarbon generation from organic matter¹². On the one hand, at the early stages of diagenesis and under the anoxic conditions, hydrogen sulphide (or polysulphides) derived from sulphate-reducing bacteria can not only react with lipids in forming the sulfur-containing compounds but also accelerate the mutual reaction of organic molecules in forming sulfur-rich macromolecular compounds such as nonhydrocarbon, asphaltene, making the lipids combined with kerogen decrease¹¹. On the other hand, sulfur can catalyze the hydrocarbon generation from kerogen.

In recent years, researches on the geological effect of sulfur are focused on the following three aspects: (i) the formation mechanism of sulfur-containing compounds, by using algae, carbohydrates, proteins, present organic matter or compounds such as β-carotene, n-octadecanol and diphenyl etc. to react with inorganic sulfur³–⁸; (ii) the characteristics of pyrolysates for the study on the origin of sulfur-rich immature oil through pyrolysis of sulfur-rich kerogen or source rocks⁹–¹⁷, and simulation of the sulphurization of hydrocarbon¹⁸–²⁰; (iii) the mechanism of pyrolysis of the sulfur-rich kerogen. It is well known that immature oil can be generated from sulfur-rich kerogen at lower temperature²¹–²², but scholars differ remarkably in their opinions concerning the mechanism of pyrolysis of the sulfur-rich kerogen. It is now commonly accepted that the weaker C-S and S-S bonds could be used to account for the generation of immature oil from sulfur-rich kerogen at lower temperatures²³–²⁴, and the immature and sulfur-rich oil from Monterey shale is such a typical example²²,²³. However, Lewan proposed a different opinion, which holds that the presence of sulfur radicals controls the catalytic effect of sulfur exists through pyrolysis experiments of kerogen with addition of sulfur.

A great number of researches have been carried out so far in regard to the geological characteristics of sulfur, and it can be reasonably postulated that the generation of oil from sulfur-rich kerogen at lower temperature was closely associated with the weakness of the C-S and S-S bonds, or the catalytic effect of sulfur. Nevertheless, no solid evidence can be found to justify these two mechanisms up to now. This is simply because these two kinds of mechanisms are difficult to distinguish through simple experiments like pyrolysis of sulfur-rich kerogen. In this paper a thorough discussion will be made as to if the catalytic effect of sulfur exists through pyrolysis experiments of kerogen with addition of sulfur.

1 Sampling and experimental

(i) Samples. The brown oil shale samples were taken from the Jintang pond in Maoming Basin of Guangdong Province, and the detailed locations of sampling are shown in the paper by Fu Jiemo et al.²⁶. The samples show a low degree of maturation and the Ro being 0.38%.

Contaminants on the outside of the samples were scraped away and the samples were washed with double-distilled water. After being dried at 40°C in the oven, the samples were pulverized to less than 200-mesh, and were extracted for 72 h in a Soxhlet apparatus with dichloromethane (DCM) methanol (93:7 v/v) in order to remove the insoluble organic matter. The kerogen was isolated from the shale via acid treatment (HF-HCl) in order to remove the mineral matter, and was purified by extraction for 72 h with dichloromethane (DCM) methanol (93:7 v/v). The composition of the kerogen is: 74.44% for C, 9.35% for H, 1.78% for S, 1.51 for atoms H/C ratio,
0.13 for atoms O/C, and 0.009 for atoms S/C ratio, which demonstrates that this kerogen is an immature Type I kerogen, and the content of sulfur is relatively low.

(iii) Experimental and analytical methods. The samples were divided into three groups: pure kerogen, kerogen with addition of sulfur ether; and kerogen with addition of sulphur. All pyrolysis experiments were performed in gold tube reactors (40 mm×4 mm id). The tubes were each welded at one end before sample loading, and 20—30 mg of samples was loaded into each gold tube. The tubes were flushed with argon for several times to insure complete removal of air. The other end of each gold tube was then welded under argon gas. The sealed tubes were put into a stainless steel autoclave and kept under a pressure of 40 MPa during the entire course of the experiment. Pyrolysis was carried out at temperatures ranging from 200 to 440°C, increased evenly for 40°C at each step, for duration of 72 h at each temperature.

In regard to the composition analyses of C$_1$-C$_5$ gaseous hydrocarbons, cleaned gold tubes were put in a vacuum system, and pierced with a needle. The gas products were released from the gold tubes and collected with a Toeppler pump for quantification purpose. After that, compositional analysis was performed through Agilent 6890N gas chromatography. External standard method was applied to the quantification of gas components, and quantification of all gaseous hydrocarbons (C$_1$-C$_5$) and inorganic gases can be carried out by one injection.

Analyses of the gases were performed on Agilent 6890N gas chromatograph with Paraplot Q type capillary column (50 m×0.53 mm id). The oven temperature remained at 70°C for 6 min, was increased from 70—130°C at 15°C/min and from 130—180°C at 25°C/min, and then remained at 180°C for 4 min. Nitrogen serves as the carrier gas, and the experiments were carried out with FID and TCD detectors at a temperature of 180°C.

In order to avoid the loss of light hydrocarbons, another gold tube was heated in parallel with the one filled with the sample at each temperature point, and was then cooled down with liquid nitrogen. After that, it was quickly cut and placed into pentane mixed with the internal standard of deuterium eicosane, and then quantitatively analyzed with HP6890 GC.

The GC conditions include a DB-5 capillary column (50 m×0.32 mm). The temperature program used was 80°C for 2 min, 80—290°C at 3°C/min and 300°C for 30 min. GC-MS was performed on a Finnigan-MAT Voyager equipped with an on-column injector and the carrier gas of helium. The interface temperature was set at 250°C. EI source, ion source temperature (250°C) and current energy (70 eV) were the conditions for the mass spectrometer. The oven used here is the same as the one used for GC.

2 Results

(i) Characterization of gas. Even though methane is the major component of the hydrocarbon gases, there are also small amounts of alkenes in addition to alkanes in the gases. Fig. 1(a) shows the changes in C$_1$-C$_5$ yields with the increasing temperature for the three groups of samples. From the figure it can be seen that the C$_1$-C$_5$ yields increase with the pyrolysis temperature. Being limited by the temperature, the maximum yields of organic gaseous cannot virtually be simulated. With the increase of pyrolysis temperature, the humidity of gas was decreased first, but was then increased and after a certain portion of temperature, it was decreased again (Fig. 1(b)).

At the maximum pyrolysis temperature 440°C, the three groups of samples can be characterized as follows:

The hydrocarbon gas yield of the kerogen is 400 mL/g TOC (Fig. 1(a)), and the H$_2$S yield is 5 mL/g TOC (Fig. 1(c)). The kerogen is of the low-sulfur type, hence the H$_2$S product yield is small, and is increased slowly with the increase of pyrolysis temperature.

The hydrocarbon gas yield of the kerogen with addition of sulfur ether is 480 mL/g TOC. In the process of pyrolysis, the gas humidity is generally big and usually bigger than 46%. When the temperature is lower than 280°C, the yield of H$_2$S increases slowly. However, when the temperature is higher than 280°C, it increases quickly. At 360°C, the yield of H$_2$S reaches 50 mL/gTOC (Fig. 1(c)), which is equivalent to the quantity that was added into the kerogen.

The hydrocarbon gas yield from the kerogen with addition of sulphur is 399 mL/g TOC (Fig. 1(a)), which is equivalent to the hydrocarbon gas yield of the kerogen, and shows a trend of variation identical to the case with the kerogen added with sulfur ether. At 360°C, the yield of H$_2$S reaches 52 mL/gTOC (Fig. 1(c)), which is equivalent to the quantity that was added into the kerogen.