

Hydrous pyrolysis transformation of organic sulfur compounds: Part 1. Reactivity and chemical changes

Zhiguang Song^{a,b,*}, Maochun Wang^a, B.D. Batts^b, Xianming Xiao^a

^a State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, CAS, Guangzhou 510640, China

^b School of Chemistry, Macquarie University, Sydney 2109, NSW, Australia

Received 7 April 2004; accepted 11 July 2005
(returned to author for revision 26 November 2004)
Available online 15 August 2005

Abstract

The geochemical transformations of a number of individual model sulfur compounds were investigated using laboratory hydrous pyrolysis under conditions of constant temperature between 200 and 330 °C and in the presence of low-sulfur brown coal. The results show that most of the compounds were reactive and could eventually be transformed largely into secondary sulfur species, whereas only aryl sulphides and condensed sulfur compounds were virtually inactive. Analysis of sulfur species in the pyrolysis products of the reactive compounds suggests that the geochemical transformation of organic sulfur could be principally characterised in terms of the formation and distribution of hydrogen sulphide, secondary sulfur compounds and macromolecular sulfur. The great variation in the proportions of secondary sulfur species indicates that there are significant differences in the geochemical behaviour of the various sulfur compounds or structures. However, as hydrogen sulphide is the predominant pyrolysis product, its formation from the decomposition of organic sulfur compounds proves to be the primary and the most significant mechanism for organic sulfur transformation during the maturation process.

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1. Introduction

The study of organic sulfur has long been one focus of organic geochemistry. The main reasons are: (1) organic sulfur is widely distributed in sedimentary organic matter and related fossil fuels, (2) it has been considered to play an important role in the generation of petroleum hydrocarbons, and (3) organic sulfur compounds have been extensively studied as biomarkers. Most of the previous studies focussed on the formation of organic sulfur

during the early stage of diagenesis, the identification of the various sulfur compounds and the possible role of sulfur in organic matter preservation and petroleum generation (e.g. Orr, 1986; Sinninghe Damsté and de Leeuw, 1989; Orr and Sinninghe Damsté, 1990; Lewan, 1998; Koopmans et al., 1998; van Dongen et al., 2003). During the past two decades, some understanding has been achieved with respect to the timing of the incorporation of sulfur into organic matter, the identification of organic sulfur compounds as biomarkers and the possible role of organic sulfur in petroleum generation (e.g. Casagrande and Ng, 1979; Casagrande et al., 1979; Valisolalao et al., 1984; Wakeham et al., 1995; Lewan, 1998; Song et al., 1998; Werne et al., 2000). However, the

* Corresponding author. Fax: +86 20 85290706.
E-mail address: zsong@gig.ac.cn (Z. Song).

precise role and reaction mechanisms of the organic sulfur functional groups are not clearly understood due to the lack of detailed knowledge of the geochemical changes involving organic sulfur during the maturation process and few studies have been carried out. One problem is caused by the large portion of organic sulfur that is chemically bonded within the framework of organic macromolecules. Currently, no direct method or technique is capable of characterising macromolecularly-bonded sulfur in sedimentary organic matter. However, a number of degradative (i.e. destructive) methods have provided an alternative approach to the investigation of the forms of organic sulfur and their transformation in sedimentary organic matter and fossil fuels.

Among these methods, laboratory hydrous pyrolysis has been the most widely used technique for artificial maturation studies of sedimentary organic matter and of individual compounds, as well as for appraising the petroleum hydrocarbon potential of source rocks (Brooks and Smith, 1969; Lewan et al., 1979; Lewan, 1985; Hoering, 1984; Comet et al., 1986; Eglinton et al., 1986; Huizinga et al., 1987a,b; Eglinton and Douglas, 1988; Smith et al., 1989, 1994; Leif et al., 1992; Rushdi et al., 2003). Major advantages of hydrous pyrolysis, compared to other thermal degradation methods, are firstly that at the relatively low temperature (<340 °C) used, cleavage of relatively weak heteroatom carbon bonds can be achieved without causing major cleavage of carbon–carbon bonds. Secondly, the pyrolysates do not contain unsaturated species (i.e. alkenes). Overall, the composition of the pyrolysates closely resembles that of naturally formed petroleum. These unique features make hydrous pyrolysis a valuable method for understanding the geochemical changes that organic sulfur has undergone during the maturation process. Many studies have used it as the main degradation approach for characterising macromolecularly bonded sulfur in kerogen and coal, as well as for studying its geochemical transformations and influence on petroleum hydrocarbon generation (Eglinton et al., 1990; Koopmans et al., 1995; Nelson et al., 1995; Lewan, 1998; Putschew et al., 1998; Song et al., 1998). However, because coal and kerogen contain a complex mixture of macromolecules in which organic sulfur exists in many types of structural forms or functional groups, the pyrolysis products only represent the bulk changes in all forms of organic sulfur rather than in an individual sulfur structure or functional group.

The chemical reactivity of a number of individual sulfur compounds under aqueous thermolysis conditions has been previously studied by a number of researchers (Katritzky et al., 1991, 1992; Ogunsola and Berkowitz, 1995) and are well documented in two papers published in 2001 (Siskin and Katritzky, 2001; Katritzky et al., 2001). Because these studies were either aimed at the

desulfurisation of sulfur-rich oil sands/tars or were intended to investigate the pure chemistry of individual sulfur compounds under laboratory aqueous thermolysis conditions, the experimental design was not aimed at simulating the chemistry of the diverse natural geochemical environment. Consequently, some of the studies employed high temperatures (>340 °C), such that the rupture of carbon–carbon bonds in target organic matter would be brought about, resulting in the formation of olefins, i.e. species which are not common in the products of natural maturation. Therefore, these aqueous thermolysis studies, although helpful for understanding chemical reactions in organic sulfur transformation, have limited geochemical application.

In the present study, by applying hydrous pyrolysis to a number of representative individual sulfur compounds in the presence of a low sulfur brown coal, we tried to quantitatively determine the sulfur species in the pyrolysate of each organic sulfur compound as a function of hydrous pyrolysis temperature and therefore to provide new information for understanding the geochemical transformation of organic sulfur, in particular the extent and significance of secondary sulfur species which evolve in the overall transformation of organic sulfur.

2. Choice of organic sulfur compounds and experimental procedures

A total of 14 organic sulfur compounds (OSCs) were selected to represent the major types of sulfur compounds or structural forms identified in coal, petroleum and sediments. The compounds cover the following types: thiophene, condensed thiophene (or aromatic thiophene), thiol (mercaptan), thiacycloalkane (sulphide), alkyl and arylsulphide and disulphide, and nitrogen-containing sulfur compounds. All these model compounds, purchased from Aldrich, were >98% pure and were used without further purification. The hydrous pyrolysis experiments were carried out mainly at four constant temperatures of 200, 230, 270 and 330 °C, but not all the OSCs were fully investigated at these designated temperatures. The names and temperatures of the hydrous pyrolysis experiments for the 14 compounds are listed in Table 1.

The experimental procedure involved transferring a certain amount of model sulfur compound containing about 20 mg of sulfur by weight, 0.5 g dried Loy Yang brown coal, cadmium acetate (in slight excess of the amount required to convert 20 mg elemental sulfur to cadmium sulphide) and 0.5 ml water into a Pyrex glass tube with a total volume of about 2 ml. The contents were mixed well by stirring with a thin steel wire. A small goblet of glass wool was used to clear the steel wire and was packed into the top of glass tube, clearing the top section of the tube to make it easier for flame

Table 1
OSCs and their hydrous pyrolysis experimental distribution

Sulfur compound	Hydrous pyrolysis temperature and experiments			
	200 °C	230 °C	270 °C	330 °C
1. Thiophene		✓	✓	✓
2. 2-Methylthiophene	✓ ^a	✓	✓	✓
3. 2,5-Dimethylthiophene	✓	✓	✓	✓
4. Pentamethylene sulphide		✓	✓	✓
5. Butyl disulphide	✓	✓	✓	✓
6. Nonyl mercaptan	✓	✓	✓	✓
7. Benzothiazole	✓	✓	✓	✓
8. 2,5-Dimethylbenzothiazole	✓	✓	✓	✓
9. 2,2'-Bithiophene		✓	✓	✓
10. Dodecyl sulphide		✓	✓	✓
11. Benzothiophene			✓	✓
12. Phenyl sulphide				✓
13. Dibenzothiophene				✓
14. Thianthrene				✓

^a ✓ Indicates hydrous pyrolysis experiment carried out at temperature indicated.

sealing. As we observed, the 0.5 ml of water was barely enough to wet the 0.5 g of brown coal and there was never a situation whereby the brown coal sample floated on the top of water. After the glass tube was sealed with a small flame, it was placed into a steel bomb of about 10 ml capacity, along with 2 ml of water and 0.5 g of the same brown coal; the aim was to equalise the pressure between the inside and outside of the glass tube. The bomb was then cap sealed. The sealed bomb was placed flat in an oven and heated at the desired temperature of 200, 230, 270 and 330 °C for 66 h. The choice of 200 and 330 °C as the starting and ending hydrous pyrolysis temperature was because, when the temperature is lower than 200 °C, there is no significant reaction of the organic matter, whereas if the temperature is higher than 330 °C, some unsaturated hydrocarbons would be generated due to carbon–carbon bond breaking. The temperature intervals were chosen to try and reflect the changes caused by increasing temperature.

After heating, the steel bomb was cooled to room temperature and opened. The unbroken glass tubes were recovered and cooled in liquid nitrogen. When frozen, they were broken and unfrozen under dichloromethane (DCM). The whole contents were removed using a small volume of methanol (MeOH) and DCM and filtered. It should be pointed out that the inside walls of the glass tubes were always clear and in mint condition, and there was never a sign of black carbon (or char) deposited on the inside wall of the tube. The solid pyrolysates were subjected to solvent extraction using a Soxhlet extractor for 66 h and a mixture of MeOH and DCM (1:9). During extraction, copper turnings were added to remove any elemental sulfur that might have been produced from the decomposition of sulfur compounds

during hydrous pyrolysis. The soluble extracts were evaporated to a small volume and retained for further analysis. The insoluble pyrolysates were then treated with hydrochloric acid to recover the sulfur trapped as cadmium sulphide by converting the cadmium sulphide to silver sulphide using a specially designed facility. After acid treatment, the insoluble coal residues were collected by filtration and their sulfur content determined by the combustion of a portion of the residues with Eschka mixture heated at 900 °C for 3 h, the sulfur being recovered as barium sulfate. The detailed method for the treatment of the insoluble residue is given by Song et al. (1998).

The low sulfur brown coal was chosen to simulate the complex natural geochemical environment and to promote all types of geochemical reaction that could involve organic sulfur during the natural maturation of sedimentary organic matter. For detailed information about the Loy Yang brown coal reference should be made to Song et al. (1998). In brief, it has a very low sulfur content (total S < 0.2%) and low ash content (1.0%). The use of this low sulfur brown coal ensured that the sulfur involved in the hydrous pyrolysis reactions was overwhelmingly sourced from the starting sulfur compounds.

Water is the liquid phase medium that evolves during the whole process of sedimentary diagenesis and is therefore considered to play an important role in the evolution of sedimentary organic matter. Although this role is not fully understood or clearly defined both in the natural process and laboratory hydrous pyrolysis, as the key ingredient in hydrous pyrolysis, water may participate as reactant and catalyst or even solvent under high temperature, as demonstrated by a number of researchers (Siskin and Katritzky, 2001 and references therein).

In our study, it was not our intention to discuss the role of water in the hydrous pyrolysis reaction or in natural processes, but by deploying the same volume of water in all the experiments it was expected that the experiments at the same temperature would be carried out under roughly the same pressure and that water effects would be comparable.

Hydrogen sulphide and elemental sulfur produced from the bacterial reduction of sulfate react preferentially with base metal (or metal cations) to form the corresponding metal sulphide (mainly iron sulphide-pyrite) during sedimentary diagenesis (Orr and Sinninghe Damsté, 1990), whereas if the sediment is depleted in metal ions, the hydrogen sulphide reacts with organic matter to form organic sulfur (Goldhaber and Kaplan, 1974; Berner, 1984; Kimblin and Johnson, 1992). Therefore, by introducing a metal compound before hydrous pyrolysis, the hydrogen sulphide or elemental sulfur produced from the decomposition of OSCs would react with metal ions preferentially to form metal sulphide. In this way the reaction between the hydrogen sulphide and organic matter to form secondary organic sulfur would be prevented. The amount of hydrogen sulphide formed could be quantified easily by determining the sulfur content in the metal sulphide formed during hydrous pyrolysis. The initial reason for selecting cadmium acetate as a reactant to remove hydrogen sulphide was because of the distinguishing colour of cadmium sulphide; furthermore it is easy to convert cadmium sulphide to other metal sulphides. However, it was borne in mind that the metal ions might be capable of accelerating the decomposition rate of some kinds of sulfur compounds reacting with aqueous solutions under subcritical temperature conditions (De Roo and Hodgson, 1978; Clark et al., 1987). There was also the controversial evidence that chromium does not reduce or liberate either organic sulfur or sulfate sulfur (Canfield et al., 1986). Considering the possible direct reaction or side affect that cadmium acetate may have on the hydrous pyrolysis reaction of OSCs, cadmium acetate was pyrolysed with water and brown coal under all the designated temperature conditions. The preliminary results of an earlier study (Song et al., 1998) suggest that cadmium acetate has little impact on the composition of pyrolysis products of sedimentary organic matter and it did not result in the formation of sulfate. Further support for this assumption was obtained from the results of a pair of pre-experimental hydrous pyrolyses on the sulfur compound thiophene in the presence of brown coal both with and without cadmium acetate at 200 °C. It was shown that the thiophene was virtually unreacted and it was fully recovered from both experiments, implying that the cadmium acetate had little influence on the chemical behaviour of the sulfur compound.

The solvent extracts were analysed using gas chromatography to identify and quantify the unreacted starting

material and the newly formed identifiable secondary sulfur compounds. The chromatograph was coupled to an electrolytic conductivity detector; helium was the carrier gas and a (J&W) DB1 column (50 m × 0.33 m) and an injector temperature of 250 °C were used. The oven was held at 40 °C initially for 4 min, heated at 4 °C per min to 300 °C and held at that temperature for 30 min.

3. Results and discussion

3.1. General reactivity of model compounds

The sulfur species and their distributions in pyrolysis products are a direct indication of the thermal reactivity and possible geochemical behaviour of the individual sulfur compounds under the simulation conditions. As described in Section 2, the sulfur species in the pyrolysates of the OSCs were considered as follows: (1) sulfur in the form of hydrogen sulphide (H₂S) trapped as cadmium sulphide; (2) sulfur incorporated into the coal matrix in the form of macromolecular organic sulfur; (3) sulfur that remained unreacted in the initial compound; (4) sulfur in newly formed secondary organic compounds. The amount of sulfur in each form was calculated and expressed as a percentage of the total sulfur in the starting compound. The percentages of these four forms of sulfur species in the pyrolysates for each model compound are presented in Tables 2–5.

It should be noted that, in addition to these four forms of sulfur species, the sulfur lost in the experimental process and in other unquantified and undetected trace sulfur gases and species including elemental sulfur was also estimated. Two particular preliminary experiments designed to identify and quantify the possible sulfur gases in the hydrous pyrolysis gas phase show that these were H₂S, CS₂ and SO₂ and that they were all present at trace levels. During solvent extraction of the pyrolysates it was noted that the copper turnings remained in their initial shining condition, suggesting that there was virtually no elemental sulfur produced in the hydrous pyrolysis when cadmium acetate was present. We estimate the sulfur in trace gases and in processing losses together would be less than 5% of the total organic sulfur involved. Therefore, the lost sulfur was not routinely determined and was ignored in the consideration of the results.

As presented in Tables 2–5, the total reacted percentage of the starting sulfur varies greatly among the 14 OSCs. There is a general tendency for the extent of reaction to increase as the temperature is increased from 200 to 330 °C. For example, at 200 °C (Table 2), only four compounds were very reactive and largely transformed into secondary sulfur-containing species, while the other OSCs remained largely inactive or only showed a small extent of reaction. As the temperature was increased to

Table 2
Sulfur distribution of OSCs after hydrous pyrolysis at 200 °C

Organic sulfur compounds	Sulfur in H ₂ S (%)	Sulfur in unreacted OSCs (%)	Sulfur in the coal residues (%)	Sulfur in the secondary compounds (%)	Total percentage of reacted OSCs (%)
1. Thiophene ^a	–	–	–	–	–
2. 2-Methyl thiophene	2.6	82.0	13.5	1.9	18
3. 2,5-Dimethylthiophene	1.5	77.4	4.5	16.6	22.6
4. Pentamethylene sulphide ^a	–	–	–	–	–
5. Butyl disulphide	55.4	Trace	5.3	39.3	100
6. Nonyl mercaptan	52.3	Trace	1.6	46.1	99.9
7. Benzothiazole	15.8	Trace	46.0	38.2	100
8. 2,5-Dimethylbenzothiazole	20.3	10.0	52.0	17.7	90.0

^a Indicates not investigated at temperature indicated.

Table 3
Sulfur distribution of OSCs after hydrous pyrolysis at 230 °C

Organic sulfur compounds	Sulfur in H ₂ S (%)	Sulfur in unreacted OSCs (%)	Sulfur in the coal residues (%)	Sulfur in the secondary compounds (%)	Total percentage of reacted OSCs (%)
1. Thiophene	6.2	88.0	3.6	2.3	12.1
2. 2-Methyl thiophene	18.3	64.0	16.1	1.6	36.1
3. 2,5-Dimethylthiophene	17.1	69.7	7.3	5.9	30.3
4. Pentamethylene sulphide	5.3	54.9	0.5	39.2	45.0
5. Butyl disulphide	59.4	Trace	0.9	39.7	99.7
6. Nonyl mercaptan	54.2	Trace	1.5	44.3	100
7. Benzothiazole	38.4	0	40.3	21.3	100
8. 2,5-Dimethylbenzothiazole	62.4	6.6	24.8	6.2	93.7
9. 2,2'-Bithiophene	6.7	56.6	25.3	11.4	43.4
10. Dodecyl sulphide	0	5.7	n.d.	>34.0	>40

n.d. means not determined.

Table 4
Sulfur distribution of OSCs after hydrous pyrolysis at 270 °C

Organic sulfur compound	Sulfur in H ₂ S (%)	Sulfur in unreacted OSC (%)	Sulfur in coal residue (%)	Sulfur in secondary compounds (%)	Total of reacted OSC (%)
1. Thiophene	27.2	63.0	6.0	3.8	37
2. 2-Methyl thiophene	53.0	26.8	17.0	3.2	73.2
3. 2,5-Dimethylthiophene	46.4	30.0	14.1	8.5	69
4. Pentamethylene sulphide	17.1	27.0	2.3	53.6	73
5. Butyl disulphide	64.1	0	2.8	33.1	100
6. Nonyl mercaptan	68.8	0	0	31.2	100
7. Benzothiazole	65.6	0	32.0	2.4	100
8. 2,5-Dimethylbenzothiazole	76.8	0	22.5	0.7	100
9. 2,2'-Bithiophene	24.7	9.1	52.0	14.2	90.9
10. Dodecyl sulphide	3.6	5.1	n.d.	>42.0	94.9
11. Benzothiophene	0.1	83.0	15.0	1.9	17

270 and 330 °C, most of the investigated OSCs had largely reacted and decomposed to produce H₂S and other forms of secondary sulfur species. Only the condensed thiophene and aryl sulphide compounds remained intact.

According to the percentages of reacted compounds as a function of hydrous pyrolysis temperature, the 14 compounds generally can be divided into three groups.

The first consists of compounds extremely reactive at 200 °C, including two nitrogen-containing OSCs, nonyl mercaptan and butyl disulphide. These compounds were largely converted to secondary sulfur species. The second group consists of thermally inactive compounds, including benzothiophene, dibenzothiophene, phenyl sulphide and thianthrene. These compounds were stable, with less than 30% of the initial material reacting at

Table 5
Sulfur distribution of OSCs after hydrous pyrolysis at 330 °C

Organic sulfur compounds	Sulfur in H ₂ S (%)	Sulfur in unreacted OSC (%)	Sulfur in coal residue (%)	Sulfur in secondary compounds (%)	Total of reacted OSCs (%)
1. Thiophene	74.3	13.5	2.0	10.2	86.5
2. 2-Methyl thiophene	73.5	14.6	2.3	9.6	85.4
3. 2,5-Dimethylthiophene	57.7	28.0	4.4	9.9	72
4. Pentamethylene sulphide	41.2	Trace	0	58.7	99.9
5. Butyl disulphide	78.0	0	9.4	12.6	100
6. Nonyl mercaptan	83.3	0	1.3	15.4	100
7. Benzothiazole	93.0	0	2.7	4.3	100
8. 2,5-Dimethylbenzothiazole	87.3	0	0.4	12.3	100
9. 2,2'-Bithiophene	64.5	0	19.1	16.4	100
10. Dodecyl sulphide	70.7	4.0	nd	22.0	96.7
11. Benzothiophene	2.4	72.4	5.2		27.6
12. Phenyl sulphide	0	95.0	0	<5	<5
13. Dibenzothiophene	0	100.0	0		0
14. Thianthrene	2.2	93.0	0	<5	7.2

n.d. – not determined.

330 °C. The third group is defined as being moderately reactive and includes the first four compounds in Table 1. They had low reactivity at the lower temperatures but eventually become more reactive as the temperature increased.

This classification generally reflects the complexity and diversity in reactivity of the compounds. The variation in the proportion of secondary sulfur species (sulfur as H₂S, in secondary sulfur compounds and in the coal residue) suggests that the geochemical behaviour of OSCs could be very complicated, depending on the types of compound and the maturation stage (hydrous pyrolysis temperature). It is clear that generated H₂S is the dominant form of secondary sulfur species for most of the reactive compounds, implying that H₂S generation is the most important feature of organic sulfur transformation. This is in agreement with the results of our previous study on the hydrous pyrolysis of organic sulfur-rich brown coals (Song et al., 1998). Furthermore, condensed sulfur compounds were virtually inactive at all temperatures and their high thermal stability explains why these compounds are often found in mature sediments and crude oils.

3.2. Effect of added functional group on reactivity

Comparison between the parent sulfur compounds and their functionalised derivatives (namely methylation) indicates that an added methyl group has multiple effects on the thermal reactivity of the functionalised compounds. For example, two methylated thiophenes (2-methylthiophene and 2,5-dimethylthiophene) appear to be thermally less stable than their parent thiophene at lower temperature, as a much higher percentage of thiophene was unreacted at 230 and 270 °C. However, at 330 °C these two methylated sulfur compounds

seemed to be slightly less reactive than their parent thiophene as they produced less H₂S and showed a smaller total reacted percentage than thiophene. There were also differences between 2-methylthiophene and 2,5-dimethylthiophene among the secondary sulfur species, as displayed in Tables 2–5. In the case of benzothiazole and 2,5-dimethylbenzothiazole, more H₂S was generated from 2,5-dimethylbenzothiazole than from the parent benzothiazole at 200–270 °C, while at 330 °C, benzothiazole produced more H₂S than 2,5-dimethylbenzothiazole but less secondary compounds than the latter.

Therefore, the effects of added functional group on the reactivity and products of functionalised sulfur compounds are very complicated and it seems that methylation would cause significant variation in the distribution of products of methylated sulfur compounds. This suggests that the types of functional groups, their number and position could all affect the chemical reactivity

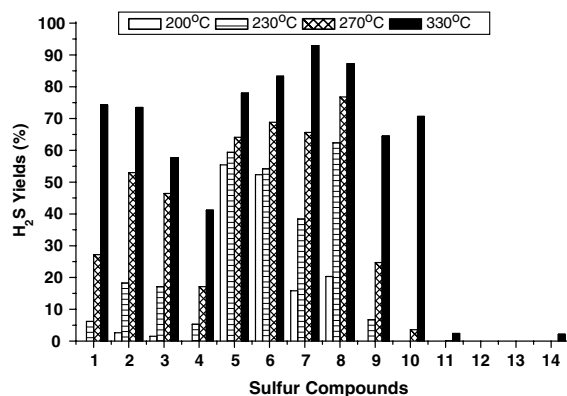


Fig. 1. Amount and distribution of H₂S generated from OSCs at 200–330 °C (see Table 1 for numbering system).

and geochemical behaviour of related sulfur compounds.

3.3. H₂S generation as a function of hydrous pyrolysis temperature

H₂S is the major product of thermolysis of organic sulfur under laboratory experimental conditions (Katritzky et al., 1991; Song et al., 1998). Therefore, the amount of H₂S generated from OSCs during hydrous pyrolysis as a function of temperature is a direct indication of the thermal stability and geochemical behaviour of these compounds. In addition to the data presented in the first column of Tables 2–5, the hydrogen sulfide generated for these 14 OSCs during hydrous pyrolysis between 200 and 330 °C is also presented graphically in Fig. 1.

Fig. 1 shows that the % of sulfur as H₂S generated from the model compounds varies greatly from com-

pound to compound as a function of hydrous pyrolysis temperature. For example, at 200 °C, the % of sulfur in H₂S generated from the reactive and moderately reactive OSCs varied from 2% to 55.4%, while at 330 °C it increased to 40–93%. Clearly, the formation of H₂S from these moderately reactive OSCs displays a generally increasing tendency as hydrous pyrolysis temperature increases. This also indicates that most of the sulfur compounds are thermally reactive and could gradually be decomposed to produce H₂S as thermal stress increased.

Fig. 2 shows the incremental results for H₂S generated from the hydrous pyrolysis of the OSCs at 200, 230, 270 and 330 °C. It also shows that the OSCs can be classified into four groups (A–D) according to the distribution of H₂S generated as a function of hydrogen pyrolysis temperature.

Group A OSCs mainly decomposed at 200 °C: this group includes butyl disulphide and nonyl mercaptan

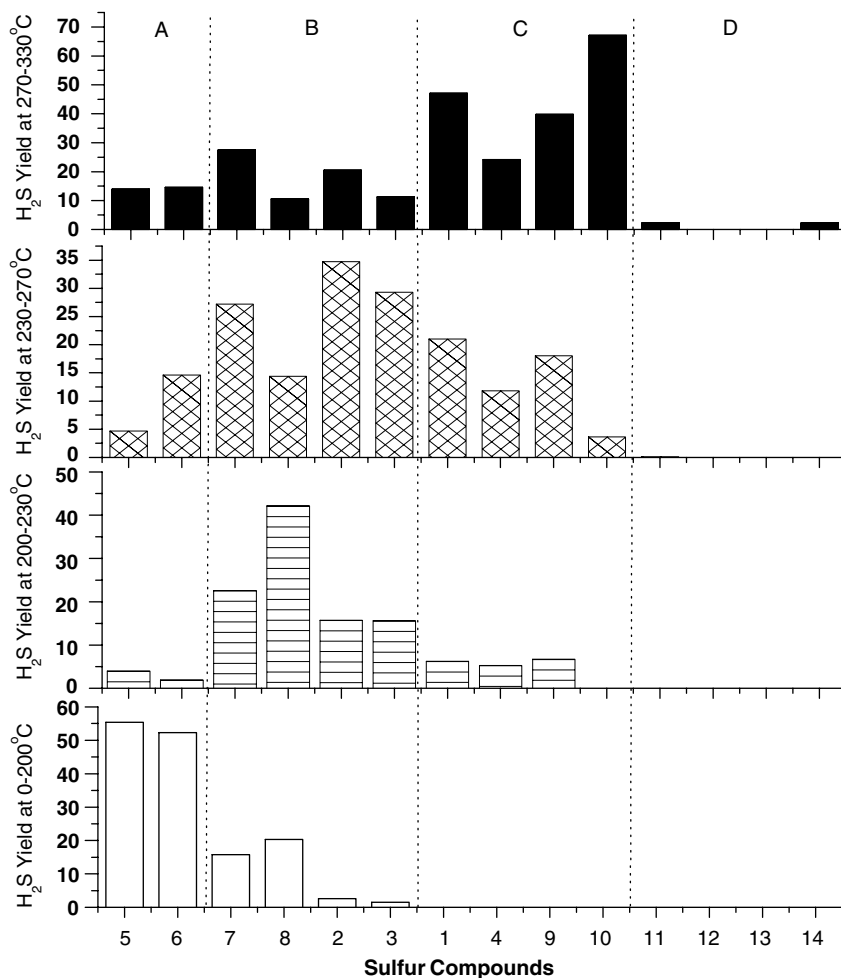


Fig. 2. Incremental distribution data of amount of H₂S generated of from OSCs from 200 to 330 °C (see Table 1 for the numbering system).

(5 and 6 in Fig. 2 and Table 1). For these two compounds, incremental data show that more than 50% of hydrogen sulfide was formed at 200 °C, whereas the total incremental change in the amount of H₂S generated at 230, 270 and 330 °C was much smaller than the amount formed at 200 °C. This implies that group A compounds may be only stable in the earlier stages of diagenesis.

Group B compounds decomposed mainly at 230–270 °C. This group includes 2-methylthiophene, 2,5-dimethylthiophene, benzothiazole and dimethylbenzothiazole (2, 3, 7 and 8 in Fig. 2 and Table 1). This group decomposed slightly to form a small amount of H₂S at 200 °C, but was mainly decomposed to form hydrogen sulphide at 230–270 °C. It should be noted that although the H₂S yields for benzothiazole and dimethylbenzothiazole maximised at 230–270 °C (Fig. 2, numbers 7 and 8), these two compounds were also very reactive as they produced a high amount of other forms of secondary sulfur species at 200 and 330 °C (Tables 2 and 5).

Group C OSCs includes thiophene, pentamethylene sulphide, 2,2'-bithiophene and dodecyl sulphide (1, 4, 9 and 10 in Fig. 2 and Table 1). These compounds were essentially stable at 200 °C and only slightly reactive at 230 °C, whereas at 270–300 °C, they were largely degraded and produced a large quantity of H₂S.

Group D compounds were virtually inert at 330 °C and included benzothiophene, phenyl sulphide, dibenzothiophene, and thianthrene (11,12, 13 and 14 in Fig. 2). They produced no or only trace amounts of H₂S at 330 °C and were almost totally recovered from the solvent extracts after hydrous pyrolysis of 330 °C. This is in agreement with the fact that these compounds (in particular, benzothiophene and dibenzothiophene as well as thianthrene) are geochemically stable compounds and are often found in mature sedimentary organic matter.

This classification is partially comparable to that obtained from the results of programmed temperature reduction (PTR) of organic sulfur functional groups in polymers by Attar and Hendrickson (1982) and Boudou et al. (1987), and the results from aqueous thermolysis on nine selective individual sulfur compounds in a number of studies (notably by Katritzky et al., 1992, 2001). However, the significant difference lies in the reactivity of the simple thiophenes, i.e. thiophene, 2-methylthiophene and 2,5-dimethyl thiophene. In the studies mentioned above, these simple thiophenes were found to be relatively inactive below 400 °C, whereas our hydrous pyrolysis study shows them to be very reactive, being largely decomposed at temperatures of 230–330 °C. The geochemical implication of this difference is obvious as these simple thiophenes are rarely found in relatively mature sediments or crude oils. This discrepancy suggests that results from thermal chemical reactions such as PTR and aqueous thermolysis cannot be fully applied to the trans-

formations of organic sulfur in the geochemical environment.

4. Conclusions

According to the above, the following conclusions may be important for understanding the geochemical transformations of sedimentary organic sulfur.

1. Most of the investigated model sulfur compounds were thermally reactive below 330 °C, with great variation in reaction rate, depending on the hydrous pyrolysis temperature. Only the condensed sulfur compounds such as benzothiophene, dibenzothiophene, phenyl sulphide and thianthrene were thermally stable, suggesting that such types of structure may be the dominant organic sulfur forms in relatively mature sedimentary organic matter.
2. The sulfur species analysis of the pyrolysates suggested that the transformations of organic sulfur compounds were actually multi-direction reactions that not only involved the decomposition of the starting organic sulfur compound but also the formation of secondary sulfur species. In general, the transformation of organic sulfur compounds could be characterised by the relative amounts of the resulting sulfur species in the pyrolysates. The great variation in the relative abundance of hydrogen sulphide, identifiable secondary sulfur compounds, organic macromolecular sulfur (the sulfur incorporated into the coal matrix) and the unreacted starting compounds suggests that there are significant differences in geochemical behaviour among these OSCs.
3. For the reactive compounds, hydrogen sulphide was, or eventually became, the dominant sulfur product among the secondary sulfur species in the pyrolysates, suggesting that the formation of hydrogen sulphide was the dominant or primary form of organic sulfur transformation under hydrous pyrolysis. This is in agreement with our earlier study on the transformation of organic sulfur in brown coals (Song et al., 1998).

Acknowledgements

This study was partially supported by the Chinese Academy of Sciences under the “100 Talent Projects”, NSFC (40373028) and an Australian Overseas Postgraduate Scholarship. Acknowledgment is also given to Dr. M.P. Koopmans and an anonymous reviewer for their pertinent comments, and to Dr. Ronald Wilkins for corrections to the manuscript.

Associate Editor—M.P. Koopmans

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