

EXPRESS LETTER

Influence of organic-inorganic interactions on the preservation of sedimentary organic nitrogen: A preliminary experimental study

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Experiments simulating reactions between pyrrole, hydrogen sulfide (H₂S), and aluminum oxide (Al₂O₃) using a dynamic thermochemical process simulator were conducted to investigate the effect of organic-inorganic interactions on pyrrolic N compounds. The results showed that N-S atomic exchange occurred at 350°C with thiophene as the main product. Thermodynamic studies indicated the reaction of pyrrole with H₂S could proceed spontaneously in most geologic settings (0–200°C). Thermochemical conversion of pyrrole into thiophene was found to be catalyzed by Al₂O₃ but inhibited by an increased volume of water. These findings suggest that conventional models may not fully account for the geochemical processes that result in the abundance and distribution of pyrrolic N compounds in sediments and crude oils. The organic-inorganic interactions in sedimentary basins may also have direct effects on the fate and preservation of pyrrolic N compounds in subsurface reservoirs.

Keywords: organic-inorganic interaction, pyrrolic N compound, alteration, N-S atom exchange

INTRODUCTION

Pyrrolic N compounds are the predominant class of nitrogen compounds normally found in crude oils and can yield much geological and geochemical information. Factors affecting the abundances and distributions of sedimentary organic nitrogen are typically attributed to the paleoenvironment of deposition (Bakr and Wilkes, 2002; Bennett *et al.*, 2004; Zhang *et al.*, 2008), thermal maturity (Clegg *et al.*, 1997, 1998; Horsfield *et al.*, 1998; Li *et al.*, 1997, 1999), source characteristics (Bakel and Philp, 1990; Clegg *et al.*, 1997; Bakr and Wilkes, 2002), migration effects (Larter *et al.*, 1996; Terken and Frewin, 2000; Zhang *et al.*, 2004; Hallmann *et al.*, 2007), as well as biodegradation (Huang *et al.*, 2003). Thus far, however, the possible influence of inorganic sedimentary ingredients upon the fate of pyrrolic N compounds has not been reported extensively. Over the past two decades, theoretical, experimental, and field studies have provided compelling evidence that the presence of water, minerals, and catalytically active transition metals in sedi-

mentary basins has the potential to substantially influence the formation and compositional evolution of petroleum (e.g., Seewald, 2001, 2003). Throughout the generation, expulsion, migration, and accumulation processes, pyrrolic N compounds are potentially exposed to various quantities of natural inorganic fluids (e.g., H₂S, H₂O) and metallic oxides (e.g., Al₂O₃, Fe₂O₃) in migration conduits and reservoirs. Water and metallic oxides are abundant components present in sedimentary rocks (Seewald, 2001, 2003). Hydrogen sulfide (H₂S), which is present in numerous gas and oil fields, is an important component of natural fluids as free gas or dissolved in reservoir fluids. Generally, bacterial sulfate reduction (BSR), thermochemical sulfate reduction (TSR), and thermal decomposition of sedimentary organic matter (e.g., oil, bitumen, kerogen, etc.) are the three main sources of hydrogen sulfide (H₂S) in hydrocarbon reservoirs. Because the nitrogen atom is more electronegative than the carbon atom, it creates an active site on the molecules of nitrogen compounds and enhances their polarity. As a result, pyrrolic N compounds may be highly reactive to inorganic sedimentary ingredients in deep burial diagenetic settings.

The objectives of this study are to examine the effect of organic-inorganic interactions on the thermal stability of pyrrolic N compounds during thermal maturation, and

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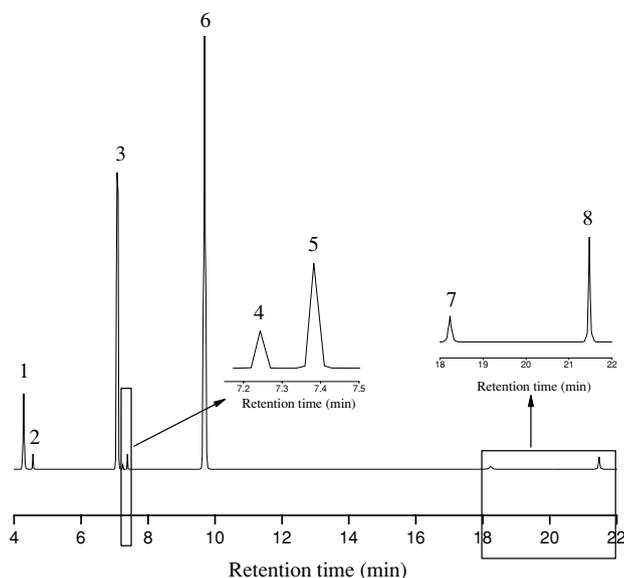


Fig. 1. Representative total ion chromatogram of oily products. Insets show expanded region with compound identification (numbers refer to major compounds in Table 1).

to tentatively discuss the related thermodynamics and mechanism. In order to address these objectives, we have designed a series of thermal simulation experiments that allow the reaction of pyrrole with H_2S and Al_2O_3 to occur under a thermal regime in which N-S atomic exchange is the dominant reaction, while thermal cracking of organic N compounds and organic S compounds is minimized. In the present study, pyrrole was used as a model compound for pyrrolic N compounds because of its simpler molecular structure compared with other pyrrolic homologues. This investigation suggests that organic-inorganic interactions could have direct effects on the geological fate of organic nitrogen compounds in deep burial diagenetic settings.

EXPERIMENTAL

Analytical grade pyrrole was purchased from Sigma-Aldrich. Aluminum oxide (Al_2O_3) was obtained from Asia Pacific Suppliers. Simulation experiments on the pyrrole- H_2S - Al_2O_3 system were conducted at 350°C for 96 h using a dynamic thermochemical process simulator (Jingzhou Ta-lin Electromachinery Manufacturing Co., Ltd., China). The simulator was made of Hastelloy C-276 alloy with a volume of 300 ml. In each run, 0.25 g of Al_2O_3 powder was placed on the bottom of the simulator, the reaction system was then evacuated, and 25.0 ml of pyrrole was loaded into the simulator through a feed regulator. The simulator was then charged with H_2S (99.9%, Shanghai Shenkai Gases Technology Co., Ltd.) until a

Table 1. Components of the oily products of the pyrrole- H_2S - Al_2O_3 reaction system ($350^\circ\text{C}/96\text{ h}$)

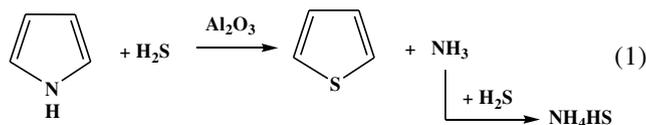
Peak No.	Retention time (min)	Compound	Formula	Relative content (%)
1	4.28	Hydrogen sulphide	H_2S	8.85
2	4.56	Isopropyl mercaptan	$\text{C}_3\text{H}_6\text{S}$	1.74
3	7.08	Thiophene	$\text{C}_4\text{H}_4\text{S}$	33.97
4	7.24	Butanethiol	$\text{C}_4\text{H}_{10}\text{S}$	0.61
5	7.38	2-butenenitrile	$\text{C}_4\text{H}_5\text{N}$	1.71
6	9.69	Pyrrole	$\text{C}_4\text{H}_5\text{N}$	51.35
7	18.24	Not identified	—	0.35
8	21.47	C_6 -sulfoether	$\text{C}_6\text{H}_{14}\text{S}$	1.42

certain pre-set pressure was reached. The initial pressure was the saturated vapor pressure of H_2S at room temperature (18°C). The final pressure of the reaction system was about 3.6 MPa. The composition of the gaseous products was determined using Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) equipped with a flame ionization detector system and Agilent headspace G1888 autosampler (Wilmington, DE, USA). Oily products were analyzed with an Agilent 6890 gas chromatograph (Agilent Technologies, Palo Alto, CA, USA) coupled with a HP 5970 mass selective detector (Hewlett-Packard, Palo Alto, CA, USA). Solid products were characterized by acid-base titration.

RESULTS AND DISCUSSION

According to the gas chromatograph and gas chromatography-mass spectrometry analysis, after the experiments, the vapor phase in the simulator was mainly composed of H_2S . A representative total ion chromatogram of the oily products is shown in Fig. 1. The individual peaks were identified by comparison of their retention index values to previously published literature, as well as by comparing their mass spectra with the Wiley 6.0 library (Wiley, New York, USA) and NIST98 (National Institute of Standards and Technology, Gaithersburg, USA) mass spectral database. The percentage composition was determined based on peak area normalization (the area of a given peak as a percentage of the sum of the areas of all peaks) without the use of correction factors. The final relative values are presented in Table 1. Thiophene and pyrrole were found to be the dominant species in the oily products (Table 1). The formation of large quantities of thiophene indicated the conversion of pyrrole into thiophene was the dominant reaction. Small amounts of H_2S , isopropyl mercaptan, butanethiol, 2-butenenitrile, and C_6 -sulfoether also appeared in the oily phase (Table 1). It should be noted that pyrolysis of thiophene above 700°C may cause the generation of H_2S . Additional blank tests on the thiophene- H_2S - Al_2O_3 sys-

tem were also carried out at 350°C for 96 h using the dynamic thermochemical process simulator. It was found that no hydrocarbons were generated in the gaseous or oily phases after the blank tests, which suggests that the decomposition of thiophene into H₂S was inhibited by the relatively low temperature and the presence of large amounts of H₂S. Therefore, the appearance of H₂S was attributed to dissolution of part of the reactant H₂S in the oily phase. The formation of isopropyl mercaptan, butanethiol, 2-butenitrile, and C₆-sulfoether was attributed to ring-opening reactions, possibly associated with thiophene and pyrrole, and they were regarded as high-temperature byproducts. Some yellow, sand-like material was found at the bottom of the simulator and had a very strong rotten-egg and ammonia odor. By acid-base titration, the yellow, sand-like material was qualitatively identified as ammonium hydrosulfide (NH₄HS). Based on the above analysis, the thermochemical reaction of pyrrole with H₂S and Al₂O₃ evidently occurred in the simulation experiments, and was characterized by atomic exchange of organic N and inorganic S. The main reaction pathway is as follows,



The thermodynamics of the pyrrole–H₂S–Al₂O₃ reaction is discussed based on reaction pathway (1). To determine the change in the chemical equilibrium for the above reaction, the effect of temperature on the standard equilibrium constant K_f^θ was calculated and is shown in Fig. 2. The related thermodynamic data were derived from Deng and Fan (1993) and Yaws (2003). In Fig. 2, the value of $K^\theta > 1$ at temperatures from 0°C to 200°C indicates that the reaction of pyrrole and H₂S could proceed spontaneously in most geologic settings with catalysis by Al₂O₃. Based on the principle of Gibbs free-energy minimization, the calculations of the reaction heat for the reaction between pyrrole and H₂S were performed with the HSC chemical software 5.0 developed by Outokumpu Research Oy. The results showed that the reaction between pyrrole and H₂S is an exothermic process in typical oil reservoirs (100–150°C), in which the heat released is estimated to be 0.39–7.65 kJ/mol pyrrole. In typical gas reservoirs (150–200°C), the reaction between pyrrole and H₂S is an endothermic process and the heat absorbed is assumed to be 0–7.40 kJ/mol pyrrole.

The conversion of pyrrole into thiophene obviously occurred at 350°C in the presence of Al₂O₃ and the conversion yield was 33.97%, which was much higher than the conversion in the pyrrole–H₂S system (6.12%). Al₂O₃ acted as a catalyst in the thermochemical atomic exchange

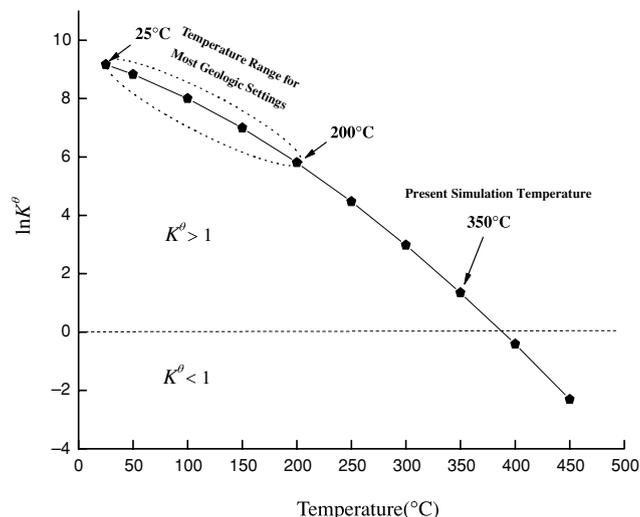


Fig. 2. Effect of temperature on the standard equilibrium constant K^θ .

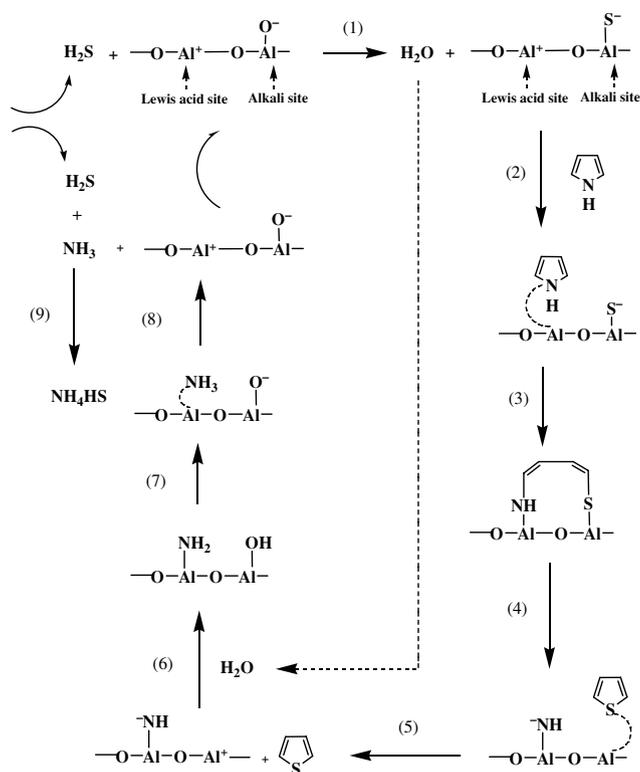
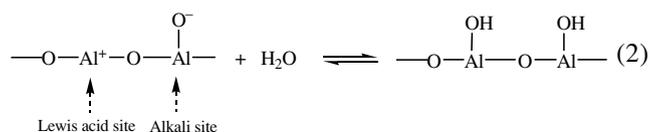


Fig. 3. Mechanism for the conversion of pyrrole into thiophene via catalysis of aluminum oxide.

of organic nitrogen and inorganic sulfur. A possible mechanism for N-S atomic exchange is illustrated in Fig. 3. The whole process consists of a series of sequential reactions involving the formation of intermediates of

pyrrole and thiophene, and regeneration of Al_2O_3 . Al_2O_3 in subsurface environments may provide Lewis acid sites and consume the molecular water generated in Step (1), allowing the overall reaction to proceed continuously. It should be noted that thermodynamic equilibration according to reaction (1) does not imply that large amounts of thiophene coexist with pyrrolic N compounds in real natural systems. To the best of our knowledge, it has been seldom documented that H_2S -rich reservoirs are more enriched with thiophene than H_2S -poor reservoirs. However, it has been proposed that reactions of oil with H_2S produce organic sulfur compounds (OSCs) with ^{34}S -enriched values, distinct from the original $\delta^{34}\text{S}$ values of sedimentary organic sulfur (e.g., Powell and Macqueen, 1984; Cai *et al.*, 2003), suggesting a possible link between H_2S and thiophene compounds in H_2S -rich reservoirs. Moreover, source rock type and source maturity may also be two other major controlling factors of thiophene concentration, but this is beyond the scope of the current work. The extent to which Al_2O_3 participates in the thermochemical alteration of pyrrolic N compounds, however, is dependent on its catalytic activity under the physical and chemical conditions likely to exist in geological environments. It was found that the presence and absence of water in the simulation experiments greatly affected the scale of the N-S atomic exchange. Although water-derived atomic hydrogen may play a central part in the reactions responsible for the primary conversion of pyrrole, the net hydrogen demand during the N-S atomic exchange is relatively minor (Fig. 3). When a large amount of water exists in the pyrrole- Al_2O_3 - H_2S system, the Lewis acid sites of Al_2O_3 can be covered by the formation of $-\text{OH}$ on the surface of Al_2O_3 particles, and the catalytic action of Al_2O_3 may be weakened accordingly. The following equilibrium between Al_2O_3 and water is assumed to exist at high temperatures,



The validity assumption was further demonstrated by the additional blank tests, in which increasing the amount of water led to a decrease in the conversion of pyrrole. Specifically, the catalytic activity of aluminum oxide would be suppressed in the presence of large amounts of water, an abundant component of sedimentary rocks. In future work, the reaction of carbazole (or benzocarbazole) with H_2S and other metallic oxides will be investigated.

CONCLUSIONS

Thermochemical atomic exchange between organic

nitrogen and inorganic sulfur evidently occurred in the pyrrole- H_2S - Al_2O_3 system at 350°C with thiophene as the major product. A thermodynamic investigation indicated that the alteration of pyrrole by H_2S could proceed spontaneously in most geologic settings (0 – 200°C) with the catalysis of Al_2O_3 . In typical oil reservoirs (100 – 150°C), the reaction between pyrrole and H_2S is an exothermic process in which the heat released is estimated to be 0.39 – 7.65 kJ/mol pyrrole. In typical gas reservoirs (150 – 200°C), the reaction between pyrrole and H_2S changes to an endothermic process and the heat absorbed is assumed to be 0 – 7.40 kJ/mol pyrrole. Thermochemical atomic exchange of organic nitrogen and inorganic oxygen is found to be catalyzed by Al_2O_3 , the Lewis acid site supplier, but inhibited by increased amounts of water. The profound effect of inorganic ingredients on pyrrole suggests that organic-inorganic interactions may represent a previously unrecognized process that could potentially have a significant influence on the chemical evolution of pyrrolic N compounds.

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