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Determination of the series of even carbon numbered *n*-alk-1-enes trapped inside geomacromolecules

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ABSTRACT

Even carbon numbered *n*-alk-1-enes, trapped inside organic geomacromolecules such as kerogen, asphaltene and solid bitumen, can survive geologic time because of the effective protection provided by the complex matrix structures of geomacromolecules. These alkenes are presumed to be derived from esters which are commonly present in various organisms. Subjected to either normal maturation increase or the impact of drastic thermal events, these trapped *n*-alk-1-enes gradually decrease in concentration and eventually disappear.

1. Introduction

Organic geomacromolecules, including humin, humic acid, kerogen, asphaltene and solid bitumen, are formed during the processes of biological organism deposition to diagenesis, kerogen cracking and petroleum production. With large molecular weight and complex structures, those geomacromolecules are separated by specific acid, alkali or organic solvents.

The *n*-alk-1-enes are geologically unstable straight chain alkenes in which the double bond is positioned at C1/C2. However, recent studies have shown that a series of even carbon numbered *n*-alk-1-enes are present in the trapped fractions of asphaltenes (Yang et al., 2009; Zhao et al., 2010, 2012; Tian et al., 2012) and solid bitumens (Cheng et al., 2012, 2013). They may be stable in these geomacromolecules owing to the protection afforded by the matrix, which inhibits transformation of the trapped *n*-alk-1-enes during later geochemical processes.

However, determination of this series of *n*-alk-1-enes inside geomacromolecules was still suspected and need more verification. As an important organic geomacromolecule, kerogen can trap some hydrocarbons in its matrix (Khaddor et al., 2008). The present work is aimed to study whether *n*-alk-1-enes can also be trapped inside kerogens, and their possible origin, geological evolution and ultimate fate are discussed. The geomacromolecules mentioned in this paper are asphaltene, solid bitumen and kerogen.

2. Materials and experimental approaches

A mudstone (from type II kerogen, with vitrinite reflectance VR_o of 0.52% and TOC of 11.0%), from the Upper Permian Lucaogou Formation of Santanghu Basin, NW China, was selected. Five mudstone samples were pyrolyzed in the semi-closed pyrolysis system (details of the system refer to Liao et al., 2004) at 80 MPa for 72 h, with 280 °C, 380 °C, 420 °C, 480 °C and 560 °C respectively. The five pyrolysis residues and the raw mudstone were treated with HCl and HF, to obtain six kerogen samples. Three solid bitumens were collected from the drilling core of Gaoke-1, Gaoshi-1 and Anping-1 wells from the Sinian Dengying Formation of Sichuan Basin, China. Their equivalent vitrinite reflectance EVR_o was between 2.35 and 2.48%.

All kerogens and solid bitumens were extracted with *n*-hexane, acetone and dichloromethane successively for 120 h, in order to preclude interference from adsorbed components. Then the extracted residues were subjected to mild oxidation to release the trapped compounds following the procedure from Liao et al. (2006). In short, bezene (20 mL) was used to transfer the extracted residues into a 250 mL flask, 30%H_2O_2 (4 mL) and CH_3COOH (15 mL) were mixed in a 50 mL beaker and slowly transferred to the

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flask with the reactants being stirred at the same time, which was carried out at ambient temperature (25 °C) with vigorous stirring for 24 h. The details of GC–MS analysis for the trapped fraction have been reported by Cheng et al. (2012). No alkenes were determined from the extracts (by *n*-hexane, acetone or dichloromethane) of any samples in the current set, and thus only alkenes that were trapped inside geomacromolecules are discussed in this work.

3. Results and discussion

3.1. Determination of n-alk-1-enes trapped inside geomacromolecules

3.1.1. Kerogens

A series of even carbon numbered *n*-alk-1-enes were the dominant constituents detected from the trapped fraction inside the raw kerogen (Fig. 1a) from the Santanghu mudstone, and the complete series of *n*-alkanes and sulfur (S_8) were detected. Even carbon numbered *n*-alk-1-enes ranged from C_{16}–C_{32} with C_{22} and C_{24} as the dominant peaks. The ratio of *n*-alk-1-ene/*n*-alkane (-ene/-ane) with the same carbon number was clearly >1.

From the 280 °C and 380 °C pyrolysis samples, only C_{18} and C_{20} *n*-alk-1-enes were detected from the trapped fraction of kerogen residues, with the ratio of -ene/-ane <1, while the complete series of *n*-alkanes and sulfur was still present in addition to some biomarkers. However, from the 420 °C or higher temperature pyrolysis samples, no alkenes were detected. The results indicate that this series of even carbon numbered *n*-alk-1-enes trapped inside kerogen (residues) gradually decreased and eventually disappeared with increasing pyrolysis temperature.

3.1.2. Solid bitumens

Cheng et al. (2012, 2013) reported that a series of even carbon numbered *n*-alk-1-enes were trapped inside some solid bitumens.

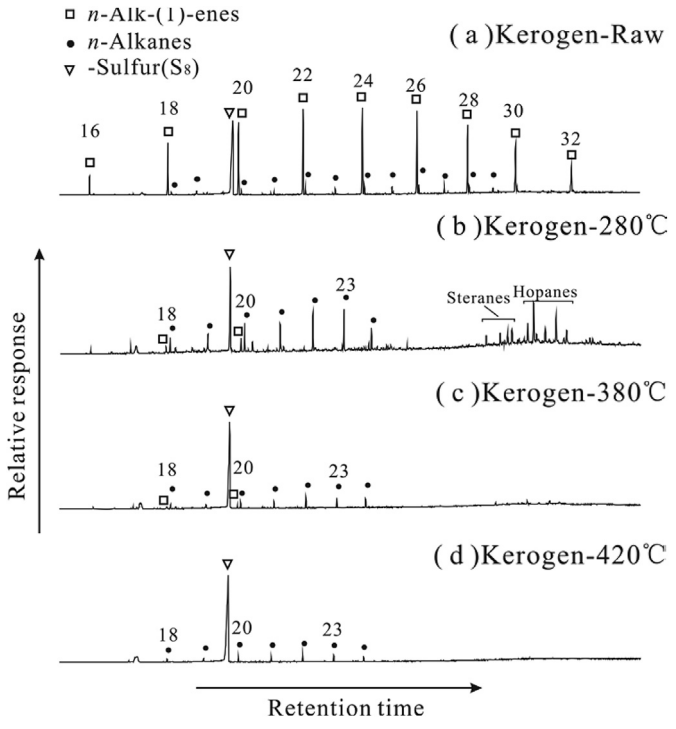


Figure 1. TIC of trapped fraction inside kerogen (residues) from different pyrolysis temperatures.

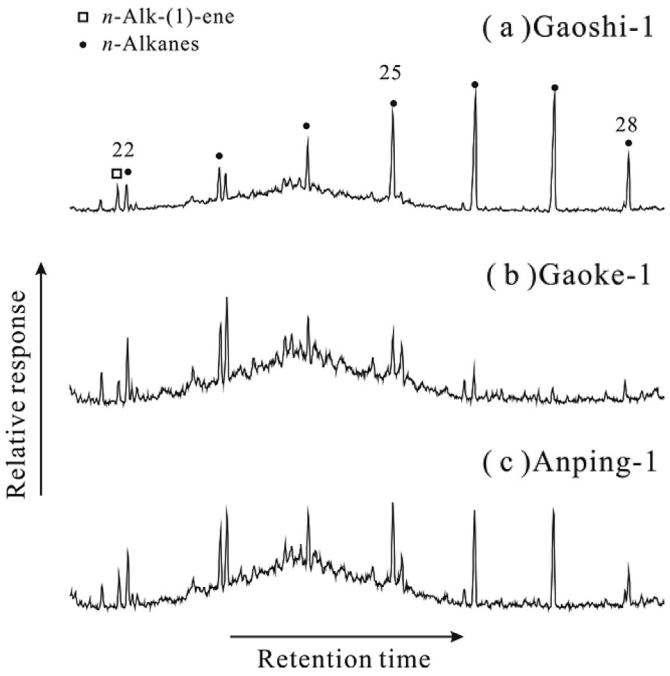


Figure 2. TIC of trapped fractions of solid bitumens from Sichuan Basin, China.

Inside the solid bitumen from the Jurassic Shaximiao Formation of northwestern Sichuan Basin, China, the trapped *n*-alk-1-enes ranged from C_{16}–C_{34} with each ratio of the paired -ene/-ane >1 (Cheng et al., 2012). From the Cambrian solid bitumens of northwestern Sichuan Basin, the trapped even carbon numbered *n*-alk-1-enes ranged from C_{16}–C_{22}, with the ratios of -ene/-ane <1 except for C_{22}- ene/-ane (Cheng et al., 2013).

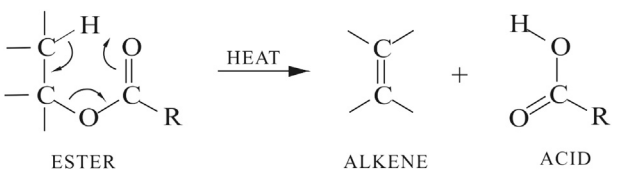
In the high maturity to over mature solid bitumens from Gaoke-1, Gaoshi-1 and Anping-1 wells, only small amounts of trapped $C_{22}H_{44}$ *n*-alk-1-ene were detected, while more *n*-alkanes were present (Fig. 2).

3.1.3. Asphaltenes

Sixteen asphaltenes from the Tarim Basin, NW China, were analyzed for trapped hydrocarbons (Yang et al., 2009), among which the series of even carbon numbered *n*-alk-1-enes have been recovered from 13 samples, which generally ranged from C_{16}–C_{30} with the ratios of the paired -ene/-ane >1. Besides these alkenes, in the trapped fraction 22,29,30-trisnorhop-17(21)-ene and 17α-hop-20(21)-ene were detected from 3 asphaltenes, and C_{23} tricyclic terp-12(13)-ene and C_{29} 18α-30-norneohop-13(18)-ene were found in another 3 asphaltenes (Yang et al., 2009). In addition, Zhao et al. (2010) reported a series of even carbon numbered *n*-alk-1-enes trapped inside the asphaltene from the ZG31 well of the central Tarim Basin.

3.2. Possible origin of this series of even carbon numbered n-alk-1-enes

Alexander et al. (1992, 1997) concluded that esters decompose under low thermal stress to yield alkenes as follows:



When a linear alkyl group connects to the alcohol side, then the *n*-alk-1-ene will be selectively formed, while the resulted acids may be integrated into the kerogen molecules again or transformed into hydrocarbons through decarboxylation. The even carbon numbered primary alcohols can be produced through the reduction of carboxylic acid (Kunst and Samuels, 2003) or acyl-CoA (Reiser and Somerville, 1997; Cheng and Russell, 2004) which commonly exists in the organisms. Esters with an even carbon numbered linear alkyl chain can be readily found in the organisms.

During the early stage of deposition under low thermal stress, early geomacromolecules such as humin, humic acid and kerogen begin to form. As the depositional processes of those macromolecules with esters proceeds, once even carbon numbered *n*-alk-1-enes were formed through the above reaction, they can be trapped inside the micropores of the geomacromolecule matrix and then preserved over geological times. With the geochemical evolution of kerogens, some trapped components could then be inherited by the subsequent macromolecular fragments such as asphaltene or solid bitumen derived from the original kerogen.

3.3. Thermal stability of n-alk-1-enes in the trapped fraction

Concentrations of even carbon numbered *n*-alk-1-enes in the trapped fraction gradually decrease and eventually disappear from the pyrolysis kerogen (residues) with increasing temperature (Fig. 1), indicating that maturity or abnormal thermal stress may seriously impact the existence of these alkenes.

Similarly, in the trapped fraction of the low maturity solid bitumens, a series of even carbon numbered *n*-alk-1-enes was determined with the paired -ene/-ane ratios generally >1 (Cheng et al., 2012, 2013). On the contrary, for the high maturity to over mature solid bitumens (EVR_o as 2.35–2.48%) from Gaoke-1, Gaoshi-1 and Anping-1 well, only a little $C_{22}H_{44}$ *n*-alk-1-ene was found with the -ene/-ane ratio <1 (Fig. 2).

According to the work from Yang et al. (2009), no *n*-alk-1-enes were detected from the trapped fractions of Tz104-CIII, Td2-Є or Ym321-Є asphaltenes. The Td2-Є and Tz104-CIII crude oils were both presumed to have undergone significant thermal alteration and the Td2 oil reservoir even has experienced a temperature of >200 °C (Zhang et al., 2004; Xiao et al., 2011). Though the thermal evolution of the oil reservoir Ym321 has not been reported, the neighboring Ym7 reservoir was reported to have experienced significant alteration (Li et al., 2010). Therefore, high thermal stress may account for the fact that no *n*-alkenes were detected from these 3 asphaltenes.

It seems that the series of even carbon numbered *n*-alk-1-enes can be generally trapped inside the geomacromolecule matrix structures. Both normal thermal maturation and abnormal thermal stress cause the alkenes to decrease in concentration and eventually disappear.

4. Summary

A series of even carbon numbered *n*-alk-1-enes were generally determined from the trapped fraction inside geomacromolecules such as kerogens, asphaltenes and solid bitumens. These *n*-alk-1-enes were presumed to be the degradation products of esters under fairly low thermal impact. These alkenes generally have a complete distribution with the ratios of paired *n*-alk-1-ene/*n*-alkane >1. Thermal maturation causes the concentration of these alkenes to decrease and eventually disappear.

Acknowledgments

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