

ALKYLATED 2,2'-BITHIOPHENES AND 2-PHENYLTHIOPHENES IN THE PYROLYSIS PRODUCTS AS MARKERS OF THE SPECIFIED LOCAL KEROGEN STRUCTURE

D. BUSHNEV

Institute of Geology of Komi SC of RAS, Pervomayskaya-54, Syktyvkar, Russia

Alkylated 2,2'-bithiophenes and 2-phenylthiophenes are known compounds of the pyrolysis products of sulphur rich kerogen. These compounds were first reported by (van Kaam-Peters and Sinninghe Damste, 1997) in the pyrolysis products of the kerogen isolated from Orbagnoux deposit. The identification was made by mass-spectra interpretation and desulphurization experiments. Then they were found in pyrolysis products of the kerogen from Upper Jurassic oil shale from Kashpir deposit by (Riboulleau et al., 2000). We had reported their presence in the pyrolysis products of S-rich kerogen of Sysola oil shale of Upper Jurassic age (Bushnev and Burdel'naya, 2003). Now we present the results of synthesis and modeling of this compounds formation.

A synthesis of 8 following compounds was carried out: 5-methyl-2,2'-bithiophene, 5-buthyl-2,2'-bithiophene, 5,5'-dimethyl-2,2'-bithiophene, 5-buthyl-5'-methyl-2,2'-bithiophene, 5-methyl-2-phenylthiophene, 5-buthyl-2-phenylthiophene, 5-methyl-2-*o*-tholylthiophene and 5-buthyl-2-*o*-tholylthiophene. To synthesize these compounds we used a number of well known techniques: Kumadu coupling to obtain biaromatic structures and alkylation through lithium derivations to prepare α -alkylated thiophene units. NMR and mass-spectra were used to confirm the compounds structures. The abovementioned compounds are related to four homologous series. And their demonstrative identification is now possible.

Earlier we supposed a scheme to explain the pathway of concurrent pyrolytic transformation of polysulphur bound n-alkyl chain depending on S-C bonds abundance (Bushnev and Burdel'naya, 2003). Due to this scheme (supported by a natural kerogens sample set with a different S_{org}/C ratios) a large number of sulphur bridges leads to formation of biaromatic pyrolysis products, and a low amount of sulphur bridges leads to mainly n-alkylthiophenes formation. For experimental verification of this scheme we performed a modeling of polysulphide bound n-alkyl chain by the polybutadiene vulcanization with elemental sulphur. The rubbers of different sulphur content were prepared by vulcanization of polybutadiene with a known amount of sulphur at 170 °C within 2 hrs.

The analysis of aromatic fractions of the pyrolysis (400 °C, 1 h) products of the rubbers set obtained showed a sharp difference between low and high sulphur-containing

rubbers. The sum of 2-n-alkyl-5-methylthiophenes and the sum of 5-n-alkyl-2,2'-bithiophenes were measured by the method of internal standard in GC-MS technique. The result is shown below (figure).

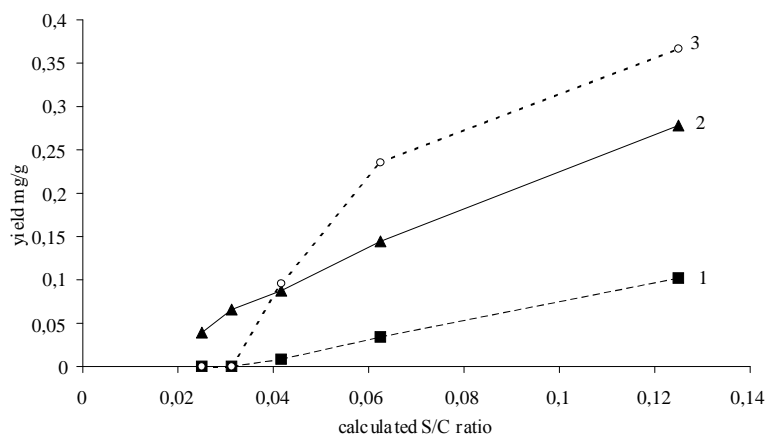


Figure 1. Dependences of the yield of sums (1) 5-n-alkyl-2,2'-bithiophenes, (2) 2-n-alkyl-5-methylthiophenes and ratio (1)/(2).

The present data allow using alkylated derivatives of 2,2'-bithiophenes and 2-phenylthiophenes in the pyrolysis products as markers of polysulphur bound n-alkyl units present in the kerogen structure.

The work is supported by RFBR project #05-05-65018

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