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SHORT COMMUNICATIONS

Note on Sulfur Removal with Metallic Copper

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INTRODUCTION

Elemental sulfur is extensively distributed in sediments and soils, whose concentration depends on the origin of the sediments and can be as high as several percent. Furthermore, sulfur is readily dissolved in most common organic solvents during extraction of organic matter from sediments and soils, interfering significantly in gas chromatography–mass spectrometry (GC–MS) or gas chromatography–electron-capture detectors (GC–ECD) [1, 2]. Hence, a cleanup procedure to remove sulfur is mandatory [3]. There are several effective methods available, of which metallic copper treatment is widely used [4, 5]. However, there is no restriction on the procedure of copper treatment. Copper can be used as powder [6, 7], granules, bars [8], or turnings [9, 10] and can be added to a Soxhlet flask mixed with extraction solvent [11, 12] or a Soxhlet thimble together with sediments during [13–15] or after [16, 17] extraction, all of which is viewed as making no essential difference. Much attention is paid to the efficiency on removing sulfur with copper, whereas its disadvantage receives little attention. Arising from our observation presented in this paper, this negligence should be noted.

Of extraction solvents, chloroform is commonly employed, in particular, in petroleum organic geochemistry. Organic matter extracted by chloroform is defined as chloroform bitumen A, which is generally separated into four fractions, i.e., saturated hydrocarbon, aromatic hydrocarbon, nonhydrocarbon, and asphaltene [18–20], and whose yields are used as indicators for evaluating the extent of diagenesis and the oil-generating potential of source rocks.

It is observed that copper powder can interact with chloroform during classical SE, even producing scores of milligrams of organic matter. Consequently, the interaction has great adverse effects on the quality and quantity of chloroform bitumen A. An investigation on the interaction was required.

MATERIALS AND ANALYTICAL METHODS

Before use, chloroform, analytical grade, was further refined and then dried over anhydrous sodium sulfate activated at 500°C overnight; copper powder, analytical grade, was treated with 10% nitric acid and then rinsed successively with distilled water, ethanol, and chloroform.

Chloroform together with copper powder was added to a flask linked with a conventional Soxhlet thimble and heated in a water bath for 72 h. The solution generated was filtered to remove copper and solvent was removed to near dryness by rotary evaporation. Products were analyzed using gas chromatography–mass spectrometry (GC–MS), ultraviolet-visible spectrometry (UV-Vis), and scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) techniques.

Analyses by GC–MS of the products were carried out on an HP6890N gas chromatograph interfaced to an HP5973N MSD quadrupole mass spectrometer. The GC was equipped with a J&W DB-5 MS fused silica capillary column (30 m × 0.25 mm, 0.25 μm film thickness); the carrier was highly pure helium gas. The column temperature was programmed at 4°C/min from 80 to 290°C and held there for 30 min. Typical MSD conditions were as follows: ionization energy 70 eV; source temperature 230°C; and quadrupole temperature 150°C. GC–MS data were acquired and processed using a Hewlett-Packard Chemistation data system. All compounds have been identified by comparisons with the NIST02L database plus interpretation of the mass spectral data. Elemental analysis was performed on a JSM-5600LV scanning electron microscope connected with energy dispersive spectroscopy (EDS). UV-Vis measurement was made using a Varian Cary100 spectrophotometer.

EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 is a total ion chromatogram (TIC) of the products generated from the interaction. The relative

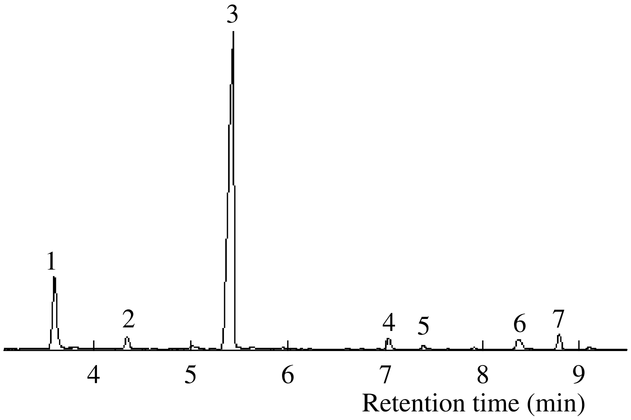


Fig. 1. The GC–MS TIC of the products (peak no. as in the table).

content of each product is calculated according to their normalized peak area. The compounds are identified by comparison of their mass spectra with the NIST02L database. The results are shown in the table.

All products shown in the table are chlorinated compounds except for three compounds remaining to be substantiated by further experiments. Compound no. 5 is not identified; however, its mass spectrum is very similar to that of compound no. 4. As a matter of fact, its main fragment ions are nearly the same as that of compound No. 4, indicating that they are probably isomeric compounds. In light of these compounds, a conclusion can be drawn that copper powder has catalysis on chloroform during SE.

To further investigate the products, it was measured with an UV-Vis spectrophotometer. As Fig. 2 shows, a strong absorption band at 247 nm is observed. According to the basic system of Woodward and the Fiesers on diolefinic absorption [21], the absorption of 1.3-butadiene (217 nm) shifts to red by 5 nm with one hydrogen atom replaced by one chlorine atom and the solvent has no effect on the absorption. The band at 247 nm is therefore assigned to a π–π* electronic transition of hexachloro–1.3-butadiene, confirming partial results of GC–MS.

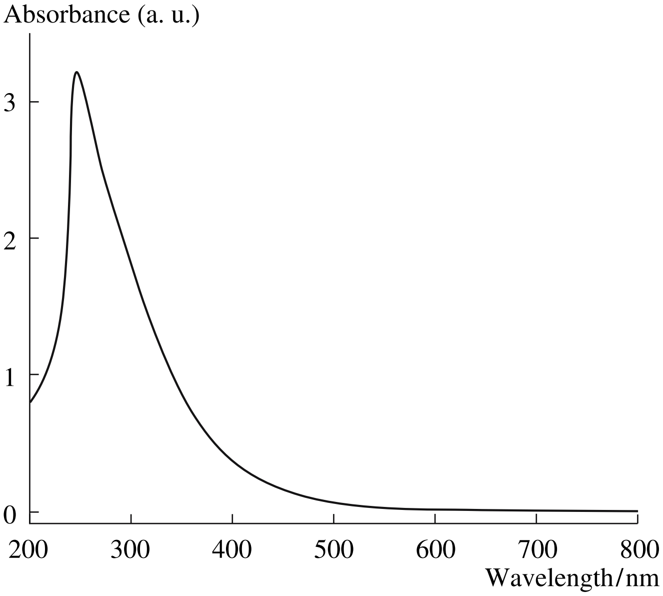


Fig. 2. UV-Vis absorption spectrum of the products.

The generation of these chlorinated compounds apparently is closely related to the presence of copper, which is confirmed by a reagent blank. The role of copper in the reaction is of importance for understanding the mechanisms involved. Then, is there copper in the products? To answer this question, we concentrate the solution of the products onto a piece of aluminum foil to analyze its elemental composition using the SEM-EDS technique. The results are displayed in Fig. 3, which contains two different scanning microareas, (a) and (b). This shows that the product is a mixture of some chlorinated and cupreous compounds. It thus indicates that copper plays dual roles in the interaction. The existing mode of copper in the products needs to be further investigated.

Analytical results of the chemical constituent of the products

Peak No.	Retention time (min)	Compound	MW	Relative content (%)	Similarity (%)
1	3.591	Pentachloroethane	200	17.51	99
2	4.335	N.I.*		2.22	
3	5.424	Hexachloroethane	234	100	91
4	7.039	2,2,2',2'-Tetrachloro-1,1'-dimethyl-1,1'-bicyclopropane	246	3.21	80
5	7.392	N.I.*.		2.86	
6	8.366	N.I.*.		2.59	
7	8.783	1,1,2,3,4,4-Hexachloro-1,3-butadiene	258	5.57	99

* N.I.—not identified.

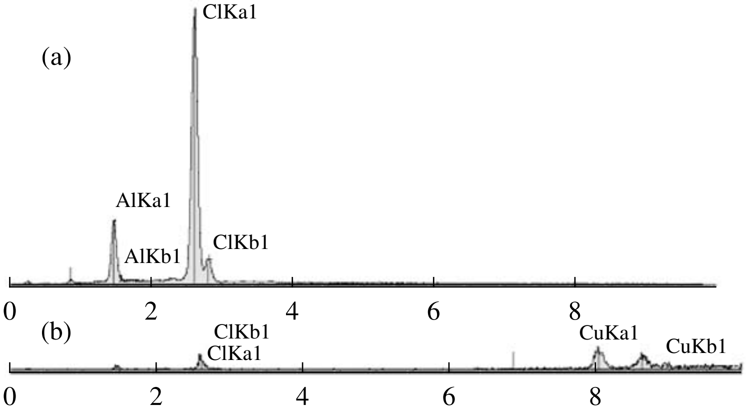
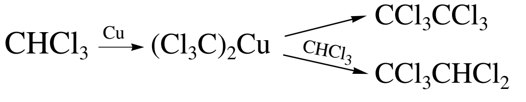


Fig. 3. EDS spectra of the products (range 10 keV).

But how should we comprehend the interaction and what is the mechanism? As we know, chloroform exhibits weak acidic characteristics [22, 23]. The chloroform molecule, possessing a slight polar character because of high electron affinity of chlorine atoms, leaves poor electron density at carbon. As a result, it probably leads to a weak electrostatic interaction of carbon with metal free electrons [24]. Considering the compounds contained in the products, it is reasonable to believe that a C–Cu bond is formed. However, it is so weak that it is only an intermediate followed by the generation of hexachloroethane. Pentachloroethane is suggested to result from interaction between the intermediate and chloroform molecules. The generation of hexachloro–1,3-butadiene may possibly be due to polymerization of dichlorocarbene. On the basis of experimental results, we propose the mechanisms shown as follows:



$$CHCl_3 \xrightarrow{Cu} (Cl_3C)_2Cu \rightarrow CCl_3CCl_3; \quad (Cl_3C)_2Cu \xrightarrow{CHCl_3} CCl_3CHCl_2$$

$$CHCl_3 \xrightarrow{Cu} Cl_2C\colon \longrightarrow Cl_2C{=}CClCCl{=}CCl_2$$

Similar results are observed in a Soxhlet apparatus devoid of air, indicating that the catalysis is independent of oxygen. And no product was detected with copper powder added to a Soxhlet thimble. In addition, sheet copper showed no distinct catalysis either. Consequently, the catalysis is dependent upon a large surface area of the powdered metal.

Despite the fact that the interaction can generate scores of milligrams of organic matter during the extraction, most of them are not detected in real sediments. Clearly, the interaction was restrained in the presence of EOM from sediments. However, some chlorinated compounds were detected and the yield of bitumen "A" increased with metallic copper added according to comparative experiments. It is safely concluded therefore that the intermediate from the interaction can interact with EOM. Moreover, these chlorinated compounds may interfere with the study of persistent organic pollutants (POPS).

CONCLUSIONS

The results obtained confirm that copper powder has an apparent catalysis on chloroform during conventional SE, resulting in the generation of a diversity of chlorinated and cupreous compounds. The quality and quantity of chloroform bitumen "A" can be influenced strongly with the input of these products. In addition, the chlorinated compounds generated may interfere with the study of POPS. Copper should accordingly be used properly and should not be added to chloroform during SE.

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