

Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65th birthday

PYROLYSIS OF NATURAL AND SYNTHETIC HUMIC SUBSTANCES

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Abstract

Thermogravimetric and Rock-Eval techniques were used for the characterization of natural (humic) and synthetic (melanoidins) substances and their hydrocarbon generation potential. A similarity between the thermal behaviour of humic substances and of melanoidins (prepared from an excess of sugar) and the unique thermal properties of melanoidins (prepared from basic amino acids) was observed. Rock-Eval analysis indicated that most synthetic melanoidins (also clay-complexed) generated more hydrocarbons and related compounds than terrestrial humic substances.

Keywords: natural and synthetic humic substances, pyrolysis, Rock-Eval technique, TG

Introduction

It is well known that humic substances account for much of the organic matter that occurs in soils, recent sediments and natural waters. Humic substances may be formed by reaction of degradation products of lignin with proteins and amino acids [1]. The 'water humus' (melanoidins) is probably formed by condensation of amino acids and carbohydrates [2-4]. Hoering [3] suggested that synthetic melanoidins and natural humic acids have chemical similarity. The apparent chemical similarity of natural humic substances and synthetic melanoidins and the important role of humic substances in kerogen formation [5] suggest that such polymers may provide model substances for studying the genesis of kerogen.

Thermal behaviour of natural and humic substances was accomplished by thermogravimetry and Rock-Eval techniques.

The shapes of the thermogravimetric curves and especially those of derivative thermogravimetry (DTG) furnish important information on the thermal stability and geochemical background of organic matter [6]. Very few comparative TG studies have been performed on biopolymers, fossilized plants, humic substances, recent and mature kerogens and coal.

Humic acid was found to be more thermoresistant than its possible precursors – lignin and cellulose [7, 8]. DTG curves showed that the main decomposition reaction of humic acids occur at 340–370 and 400–420°C. Thermogravimetric studies on the decomposition of humic and fulvic acids under air [9, 10] revealed that low-temperature peaks result from the elimination of functional groups, whereas the high-temperature maxima are due to the decomposition of their ‘nuclei’.

Although the source of starting materials and mechanism of formation of natural humic substances are still matters of controversy, the condensation of reducing sugars and amino acids has been postulated as a possible humification process in soils and especially in marine environment [11, 12]. It has been suggested that synthetic melanoidins and natural humic acids have close chemical similarity [3, 13, 14]. Orsi [15] studied the thermal behaviour of sugar and amino acid mixtures.

Experimental

The melanoidins were prepared by condensation of amino acids and carbohydrates in hot alkaline solution (Hedges, 1978). The crude products were filtered through a Whatman No. 42 filter paper and purified by continuous dialysis followed by lyophilization. The isolation and purification of humic acids were performed as described by Ioselis [16].

Thermogravimetric data were obtained on a Mettler thermobalance. The samples (containing 25 mg of organic matter) were crushed to 100–150 mesh and heated in a platinum crucible from 80 to 800°C at 6 deg·min⁻¹ under pre-dried N₂ (40 ml/min). All samples were preheated at 80°C to constant weight prior to pyrolysis.

Infrared spectra were recorded using a Perkin-Elmer Model 180 i.r. spectrophotometer. Thoroughly dried samples (about 1.4 mg) were compressed with KBr under 10 atmospheres pressure. The discs were dried over P₂O₅ in a desiccator, or in an oven at 80°C.

The quantitative estimation of the melanoidins and HHA ‘productivity’ as potential hydrocarbons producers (HE) was conducted using the Rock-Eval technique pyrolysis at 600°C for 15 min in an inert atmosphere. The term HE

describes the hydrocarbon part of the pyrolyzed products detectable by flame ionization detector (FID) [18].

A similar series of experiments was performed with physical mixtures of wet complexes of humic acids and melanoidins with several minerals. Physical mixtures were prepared by thorough grinding of organic matter with clays (kaolinite and montmorillonite). Wet complexes were prepared by lyophilizing aqueous solutions of clay-organic matter complexes. Most samples (described in Table 1) of about 50 mg each, were placed in a small porcelain crucible and pyrolysed at 600°C for 15 min in inert atmosphere. The Rock-Eval analyses were performed at the Chevron Oil Field Research Company, La Habra, California.

Table 1 Natural and synthetic substances: Mel – Melanoidin; Mel_H – Melanoidin fraction precipitated at *pH* 2; Mel_F – Melanoidin fraction soluble at *pH* 2

Sample No.	Substance	Molar ratio
1	Mel: Galactose–Lysine	1:9
2	Mel: Galactose–Lysine	1:1
3	Bovine Albumine	
4	Mel: Glucose–Methionine	1:9
5	Mel: Galactose–Lysine	9:1
6	Mel _F : Glucose–Valine	9:1
7	Mel: Glucose–Tyrosine	9:1
8	Mel: Glucose–Cystine	9:1
9	Mel _F : Glucose–β-Alanine	9:1
10	Fulvic acid	
11	Mel _H : Glucose–Valine	9:1
12	Mel: Galactose–Glycine	9:1
13	Mel: Galactose–Glycine	1:1
14	Mel _H : Glucose–β-Alanine	9:1
15	Humic acid (debitumenized)	
16	Humic acid	

Results and discussion

The influence of *pH* on the thermal stability of humic substances was studied. A similarity in thermal behaviour of natural humic substances and of melanoidins (prepared from an excess of sugar) and the unique thermal properties of melanoidins (prepared from basic amino acids) was observed. Extraction and purification of HA, preparation of melanoidins and the details of the TG analysis were described by Ioselis [16].

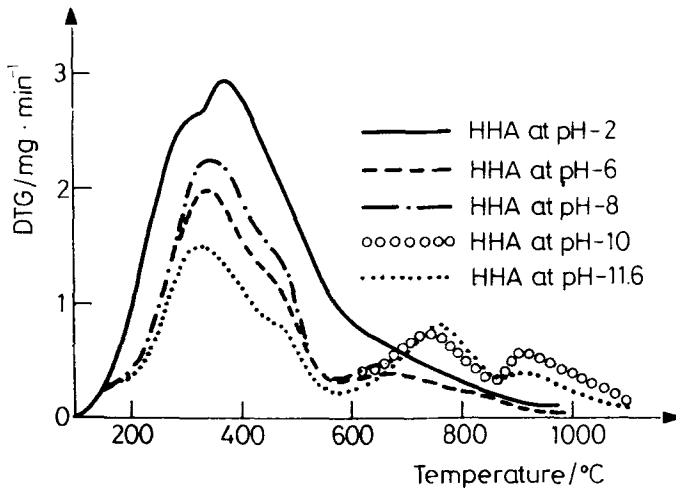


Fig. 1 DTG of Hula Humic Acid (HHA) at various pH values

Figure 1 shows DTG curves of several basic complexes of HHA, and a sample of Hula Humic Acid (HHA) which was precipitated at pH 2. The following observations were recorded:

1. a major weight loss occurred around 330°C .
2. there is an increase in the 740°C peak and emergence of a new peak at 900°C for basic complexes of HHA (Fig. 1).

In order to explain the changes in DTG curves with the change of the pH of the environment of the complexes some relationship between DTG and titration curves of humics had to be considered. Narkis and Rebhun [17] reported that the titration curves of most humic acids can be separated into the following three zones. In the first zone ($pH < 4-5$), the COOH groups are dissociated, the third zone relates to pH values higher than the pK values of 8-9 typical for phenols and probably represents the dissociation of phenolic and/or other acidic groups of similar pK values. The zone located between pH 5 and 8 is an intermediate one, where ionization of carboxylic and phenolic groups overlap. The infrared spectra of HHA and some of its 'basic' complexes confirm the 'titration behaviour' of COOH groups and gives clear evidence of ionizing carboxyl groups already at pH 6 (Fig. 2).

The first and the largest DTG peak is maximized at about 300°C for pH values lower than 4-5. It is noteworthy that the first and the main thermal destruction zone peak stems from the decomposition of the free non-ionized carboxyl and phenol groups as well as from carbonyl and alcoholic groups, which are not affected by change in pH .

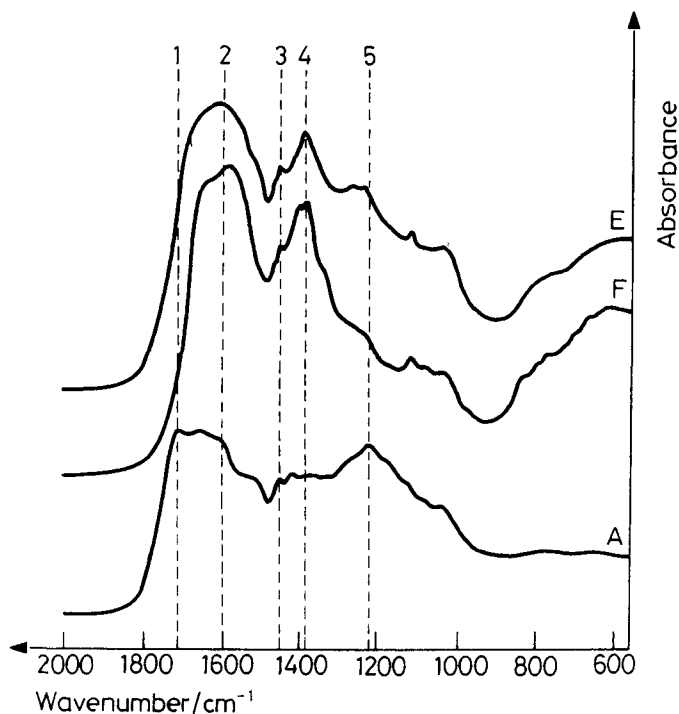


Fig. 2 Infrared spectra of humic acid and its 'basic' complex 1 - CO of COOH and/or of ketonic stretch; 2 - COO⁻ antisym. band; 3 - carbonate peak; 4 - COO⁻ sym. band; 5 - CO stretch. A = Hula Humic Acid (HHA) E = HHA at *pH* 6, freeze-dried F = HHA at *pH* 11.6, freeze-dried (prepared in inert atmosphere)

The infrared spectra of HHA and its corresponding complexes, pyrolyzed at 450°C (Fig. 3) obviously shows that HHA which was precipitated at a low *pH* value undergoes almost complete destruction of the bulk of the functional groups. The 'basic' HHA complexes demonstrate definite thermal stability at 450°C. The zone at 470°C stems from HHA (in *pH* range of 6–8) is probably due to the ionized carboxyl groups. The zone at 740–750°C is characteristic for HHA at *pH* higher than 8–9 and may be due to the ionized phenolic moiety. The peak at 900°C originates from carbonates, which are precipitated during the preparation of the 'basic' complexes.

It was found that aliphatic and aromatic moieties in HHA remained almost unchanged even after pyrolysis at 800–900°C under inert atmosphere.

Heat treatment at 650°C of HHA for 15 min yielded volatiles, such as CO₂, acetone, furanes and related heterocyclics, which correspond to 40% of the initial carbon of HHA. These products have probably been derived from the pe-

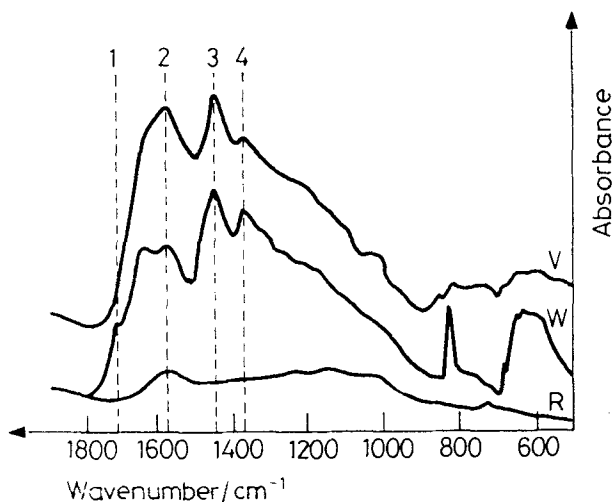


Fig. 3 Infrared spectra of humic acid and basic complex after pyrolysis. 1 - CO of COOH and/or ketonic stretch; 2 - COO⁻ antisym. band; 3 - carbonate peak; 4 - COO⁻ sym. band. V = 'E' after heating at 450°C during 0.3 h; W = 'F' after heating at 450°C during 0.3 h; R = HHA after heating at 450°C during 0.3 h

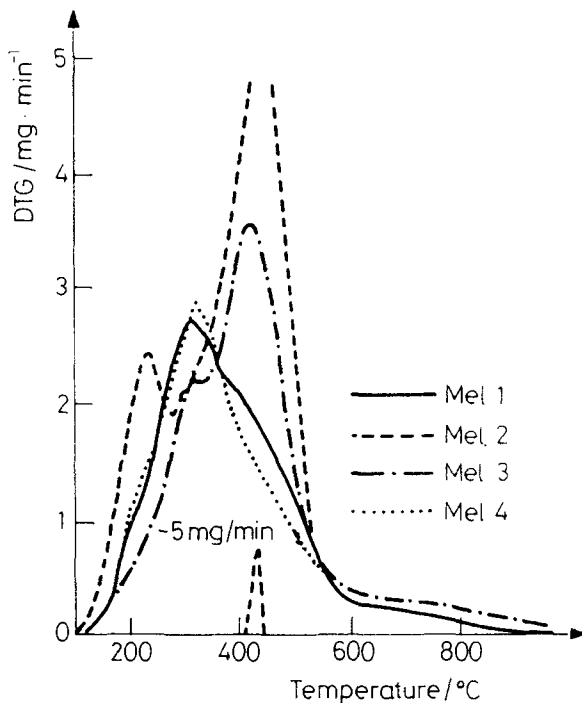


Fig. 4 DTG of melanoidins MEL-1 Galactose-valine (9:1) MEL-2 Galactose-lysine (1:1) MEL-3 Galactose-arginine (1:1) MEL-4 Galactose only (pseudomelanoidin)

ripheral functional groups of HHA [17]. Pyrolysis of basic complexes of HHA under similar conditions afforded volatiles corresponding to about 20% of the initial carbon.

Figure 4 represents DTG curves of some melanoidins: MEL-1 was prepared from an excess of sugar and neutral amino acid (valine), MEL-2 and MEL-3 were synthesized from sugar and a basic amino acid (lysine and arginine) in a molar 1:1 ratio, MEL-4 was prepared from sugar only. Examination of Fig. 3 reveals that melanoidins which were prepared from sugar only (pseudo-melanoidins) and those from an excess of sugar behave similarly to natural humic acids. This observation further supports the remarkable similarity of humics and melanoidins [16] and emphasizes the special importance of sugar as starting material in the formation of humic substances.

Melanoidins which were prepared from sugars and basic amino acids decomposed at about 420°C. This might be due to the fact that during the reaction of sugars with basic amino acid crosslinking through the 'extra' amino groups may take place.

Most of the synthetic melanoidins generate more hydrocarbon equivalents (HE) than terrestrial humic substances on pyrolysis (Fig. 5). The HE yield of

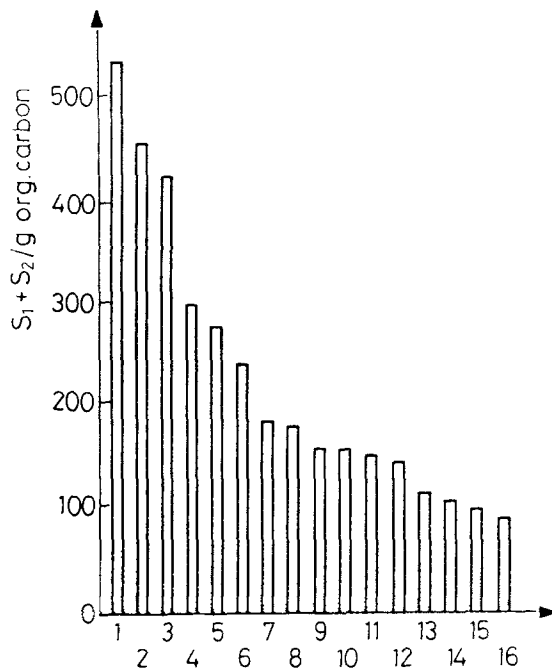


Fig. 5 Comparison of hydrocarbon equivalents obtained by Rock-Eval pyrolysis of humic substances and melanoidins

melanoidins depends on the type of the amino acid and amino acid-carbohydrate ratio.

It appears that natural humic substances and melanoidins synthesized from an excess of carbohydrates may be correlated to kerogen obtained from peat [19]. Melanoidins synthesized from excess amino acids have HE values close to immature type-II kerogen.

There is a possibility that the increase in the HE values of melanoidins is due to the presence of lone pairs of electrons on heteroatoms (e.g. lysine, cystine) which probably generate free radicals during pyrolysis and also the length of the carbon chain, or a combination of these factors. In relating HE values of immature organic matter to kerogen we should take into consideration the MW (molecular weight), the presence of sulfur and nitrogen and many functional groups in the organic matter.

Another interesting observation of this study is that the physical mixture of kaolinite and organic matter generated on average about 35% more HE than the corresponding mixtures with alumina and montmorillonite (Fig. 6).

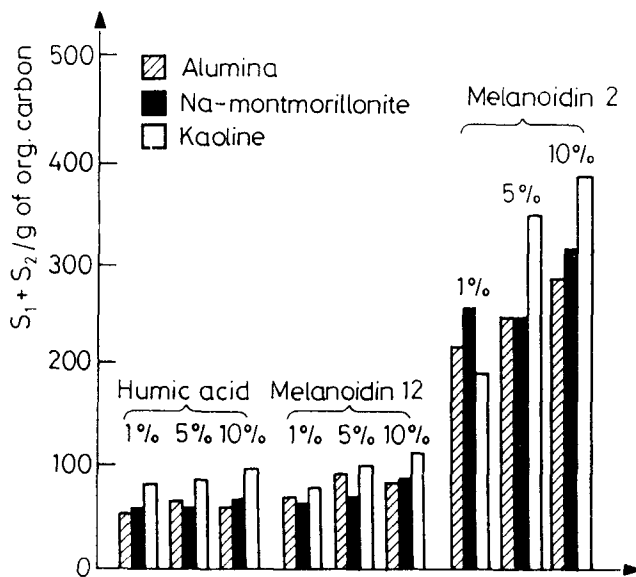


Fig. 6 Hydrocarbon equivalents (mg) obtained by Rock-Eval pyrolysis of humic acid and melanoidins in the presence of minerals

Conclusions

It has been shown that DTG curves provide important information on the nature of several synthetic and natural humic substances. It was found that the

three regions off ionization of functional groups affect the thermal behaviour of humic acids; the ionization of carboxylic and especially phenolic groups leads to an increase of the thermal stability of humic acids. The thermal stability of melanoidins which were prepared from sugar only and those from excess of sugar over amino acid is similar to that of humic acids. Melanoidins synthesized from basic amino acids possess higher thermal stability.

Pyrolysis (Rock-Eval) of synthetic melanoidins usually generated more hydrocarbon equivalents (HE) than the terrestrial humic substances. The HE yield of melanoidins depends on the nature of the amino acid and the amino acid-carbohydrate ratio. Kaoline-organic complexes yielded more HE than the corresponding montmorillonite complexes.

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Zusammenfassung — Thermogravimetrische und Rock-Eval-Techniken wurden zur Charakterisierung von Natur- (Humin-) und synthetischen (Melanoidin-) Substanzen und deren Fähigkeit zur Kohlenwasserstoffgenerierung benutzt. Es wurde eine Ähnlichkeit im thermischen

Verhalten von Huminsubstanzen und (aus überschüssigem Zucker hergestellten) Melanoidinen und den thermischen Eigenschaften von (aus den entsprechenden Aminosäuren hergestellten) Melanoidinen beobachtet. Eine Rock-Eval Analyse erwies, daß die meisten synthetischen Melanoidine (auch als Tonerde-Komplex) mehr Kohlenwasserstoffe und ähnliche Stoffe generieren als natürliche Huminsubstanzen.