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THE ROLE OF VARIOUS COMPOUNDS IN HUMIC ACIDS STABILITY STUDIED BY TG AND DTA

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Simultaneous DTA/TG technique has been used to study the influence of various model compounds (aromatics, organic acids, alkanes, ketone, heterocyclic and sterole) on the thermo-oxidative behavior of lignite humic acids. As a measure of stability the shift of the onset temperature of the exothermic degradation peak has been used. Further, the ratio of mass loss recorded in the high and low temperature ranges (thermogravimetric index) was used to evaluate the role of added compounds on the recombination reactions occurring during the thermooxidative degradation of humic acids. It has been demonstrated that most of added compounds play a role during those processes at relatively low concentrations (1% mass/mass) and affect the humic acid stability as well as the value of thermogravimetric index (i.e. the degree of the apparent aromaticity). It has been clearly shown, that the latter parameter reflects more the 'qualitative' than the 'quantitative' relationship between biodegradable humified parts in the extracted pool of organic matter.

Keywords: *DTA, lignite humic acids, TG, thermogravimetric index, stability*

Introduction

Methods of thermal analysis (TA) represent rapid, accurate and interference-free approach very attractive also in the investigation of such complex materials as humic acids (HA) and related humified substrates [1–7]. It is generally accepted that HA consist of a huge number of miscellaneous compounds formed as a result of microbial attack to the dead plant tissues and animal bodies as well as their chemical decay. HA represent a complex mixture of amphiphilic, both aliphatic and aromatic, molecules held together by weak interactions and playing specific roles in natural systems [8]. Manifestation of individual compounds or groups in the TA record of the HA mixture cannot be easily rationalized. Consequently, employing TA techniques for the HA characterization, only basic parameters such as the peak temperatures, mass losses in specific temperature regions or their ratio [9], peak onset temperatures and similar parameters of degradation kinetics [3, 5] or temperatures of glass transitions [7] have been most frequently reported.

It is generally agreed that the process of HA thermal or thermo-oxidative degradation proceeds in two or three steps [6]. In the lower temperature range, aliphatic molecules, many polar groups and simple aromatics are degraded. The second step (in the temperature range ~200–300°C) is usually ascribed to the decay of polyaromatic moieties. The third step (>400°C) reflects the degradation of polyheterocyclic structures. From the chemical degradation studies, however, there is no convincing evidence for the presence of condensed aromatic components in humic structures [10]. Moreover, some studies indicated that the aliphatic molecules tend to recombine to form more stable aromatic structures in the course of degradation [11]. Hence, it is probable that the character of processes occurring during the first step has a strong influence on the second and third one. As a measure of stability the so-called thermogravimetric index (TGI) , i.e. the ratio of mass losses in the above mentioned temperature regions, is frequently applied [10]. Apparently, TGI value can be more or less biased by the presence of small amount of any molecule.

The aim of this work was to study the effect of various compounds on the basic TG and DTA parameters of the HA thermo-oxidative degradation and to elucidate relation of the HA structural features to their TA behavior.

Experimental

Humic acids

HA were extracted from lignite obtained from the mine Mír located in the southern part of Moravia (Czech Republic) nearby Hodonín in 1998. Details concerning the lignite and extracted HA can be found in [12–14]. Fraction of the lignite captured between the 0.2–0.3 mm sieves was mixed with the aqueous

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NaOH solution (0.5 mol dm^{-3}; 1:10) and stirred for 3 h. After centrifugation, the supernatant was treated with the concentrated HCl until pH was about 1 in order to precipitate the humic acids (fraction HA). HA were then treated with 0.5% (v/v) HCl-HF solution overnight to remove residual ashes, dialyzed (Spectra/Por® dialysis tubes, 3500 Mw cut-off) against distilled water until chloride-free.

The HA, still in the gel-like state (pH=4.2), was divided into portions of 5 mL. A portion was dried to constant mass to determine the content of dry humic acids, which then served to calculate the amount of model compounds added to the HA in concentrations 1 and 10% (mass/mass). As model compounds the following substances were selected (abbreviation of resulting mixture are given in parentheses): ethanol (HA1), octanol (HA2), glycerol (HA3), heptane (HA4), cyclohexane (HA5), cyclohexanone (HA6), formic acid (HA7), acetic acid (HA8), propionic acid (HA9), palmitic acid (HA10), benzoic acid (HA11), phenol (HA12), benzene (HA13), benzoyl peroxide (HA14), *p*-xylene (HA15), *p*-cresol (HA16), *m*-cresol (HA17), pyrocatechol (HA18), hydroquinone (HA19), pyridine (HA20), cholesterol (HA21). The symbol of a sample is extended with the affix –1 or –10 to denote mixture concentrations 1 or 10%. If a solid model compound was used, it was finely milled before the addition. Each sample containing wet HA with the added model compound was shaken for 48 h at the room temperature, dried in an oven at 30°C, homogenized in an agate mortar and stored in a desiccator above NaOH.

Thermal analysis

Shimadzu DTG-60 was employed recording simultaneously thermogravimetry (TG) and differential thermal analysis (DTA) curves. The temperature scale was calibrated using melting of In and Zn. Before each measurement, the humic samples were carefully homogenized in an agate mortar. The measurements were carried out in an open platinum crucible at the heating rate of 10°C min^{-1} from the room temperature up to 600°C. The mass of samples was approximately 2 mg. Oxygen was used as a purge gas with the flow rate 20 mL min^{-1}. The measurements were repeated three times for each sample and the highest standard deviation for the temperature onsets (T_o) was ±0.4°C whereas that for TGI±0.06. Parameters used for evaluation of differences among the humic samples were the peak temperatures, onset temperature, and the mass losses in the temperature regions corresponding to the individual degradation steps.

Results and discussion

The TG and DSC records of HA extracted from South Moravian lignite can be found in [7]. Changes of the published records in comparison with those obtained in this work (Fig. 1) can be attributed to the lignite ageing processes. The most important ageing factors can be the influence of atmospheric oxygen, humidity and microbiological attack. As a result, the cleavage of the first DTA peak and the shift of the temperature of the second one can be seen. Records of all modified samples are not reported. In the case of any significant change a note is given in the corresponding table or in the following text. The parameters obtained from the DTA and TG measurements are summarized in Tables 1 and 2 for 1 and 10% samples, respectively. Temperature regions in Fig. 1 are divided into four groups; the region A corresponds to the moisture evaporation, B to the degradation of aliphatic and some aromatic structures (i.e., the biodegradable part), C and D to the degradation of aromatic and heterocyclic structures, respectively (the humified part).

Another important parameter reported in Tables 1 and 2 is TGI corresponding to the percentages of the mass losses in regions C and D divided by the mass loss in region B. The onset and endset temperatures of regions were determined by differentiation of TG records.

As can be seen, the presence of model compounds affected all determined TA parameters but no clear dependence can be observed. However, some general conclusions can be drawn.

Addition of alcohols

As can be seen in Table 1, 1% ethanol (HA1-1) and octanol (HA2-1) addition to the HA caused increase of the onset temperatures whereas in the case of 10% samples the effect was opposite. Glycerol (HA3-10) treated samples, on the other hand, showed different

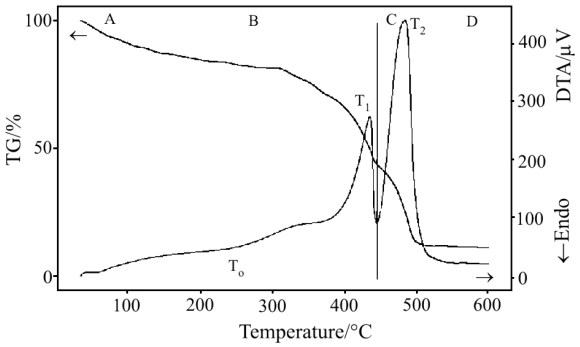

Fig. 1 DTA/TG record of HA. A – water evaporation, B – evaporation of volatile fractions and degradation step (aliphatics, simple aromatics), C – degradation step (aromatics), D – degradation of N-polyheteroaromatics

Table 1 Parameters obtained from simultaneous DTA/TG records for 1% enriched samples. T_o is the onset temperature of degradation, T_1 and T_2 stand for the peak temperatures of the first and second degradation step, respectively. TGI was calculated as the ratio of mass losses in temperature regions corresponding to second (C), third (D) and first degradation steps (B)

Sample	Abbrev.	Sample mass/mg	DTA/°C			TG–mass loss/%				Total loss/%	TGI index
			onset	T_1	T_2	A	B	C	D		
pure HA	HA	1.78	238.9	415.9	470.8	8.9	43.8	32.6	2.6	87.9	0.80
Alcohols											
ethanol	HA1-1	2.14	239.2	411.0	476.0	10.4	32.2	29.0	8.3	79.9	1.16
octanol	HA2-1	1.91	242.7	411.3	472.8	11.9	42.2	32.6	1.9	88.6	0.82
glycerol	HA3-1	2.21	237.9	413.4	474.7	10.4	43.0	35.3	2.2	90.9	0.87
Alkanes											
heptane	HA4-1	2.00	235.8	414.4	473.8	10.1	43.5	32.3	2.4	88.3	0.80
cyclohexane	HA5-1	1.88	237.1	414.0	474.8	11.2	45.8	29.3	3.3	89.6	0.71
Ketone											
cyclohexanone	HA6-1	2.16	234.4	411.4	480.5	5.9	30.9	34.0	1.6	72.4	1.15
Organic acids											
formic acid	HA7-1	1.68	236.6	411.9	474.6	3.5	44.6	34.4	7.1	89.6	0.93
acetic acid	HA8-1	2.00	236.6	413.1	475.6	9.3	46.0	37.1	0.9	93.3	0.83
propionic acid	HA9-1	1.79	241.9	420.1	466.1	7.2	50.7	31.3	4.6	93.8	0.71
palmitic acid	HA10-1	2.01	240.7	417.4	474.3	3.1	35.0	30.9	2.5	71.5	0.95
benzoic acid	HA11-1	1.68	243.7	406.3	469.2	11.4	37.9	31.0	5.2	85.5	0.95
Aromatic compounds											
phenol	HA12-1	2.11	236.9	414.3	474.9	9.9	39.2	29.2	3.2	81.5	0.83
benzene	HA13-1	2.08	238.6	408.8	472.5	9.5	41.3	26.5	6.2	83.5	0.79
benzoyl peroxide	HA14-1	2.20	243.5	415.3	469.1	8.0	48.6	29.3	2.8	88.7	0.66
p-xylene	HA15-1	2.02	242.8	416.8	479.0	5.7	37.0	35.8	3.3	81.8	1.06
p-cresol	HA16-1	2.24	236.0	412.7	476.8	6.6	46.2	35.5	1.4	89.7	0.80
m-cresol	HA17-1	2.06	238.2	413.8	474.8	8.7	45.9	31.2	3.8	89.6	0.76
pyrocatechol	HA18-1	1.88	237.2	415.8	476.5	8.7	39.8	34.5	3.1	86.1	0.94
hydroquinone	HA19-1	1.69	239.6	408.6	474.3	9.7	42.8	34.5	3.4	90.4	0.89
Heterocyclic compound											
pyridine	HA20-1	1.61	233.2	412.1	467.5	11.4	44.0	21.1	1.6	78.1	0.51
Sterole compound											
cholesterol	HA21-1	1.92	239.5	421.0	465.0	9.9	50.8	24.1	0.7	85.5	0.49

behavior. The TGI determined as the ratio of mass loss in the regions C and D to the mass loss in the region B showed an increase in the case of 1% addition and decrease in the case of 10%. It is known that HA possesses a high number of carboxylic and ester groups in their molecules. The former can easily react with added alcohols to form esters [15]. The unreacted excess of alcohol present in the sample was then either evaporated during the drying process or TA analysis or reacted via transesterification reactions with the HA forming esters [16]. Mass loss reported in Tables supports the hypothesis of evaporation during TA analysis. Moreover, DTA record of the sample HA2-10 showed more peaks than the original HA sample. It can be supposed that carbon chains of different lengths and different molecular arrangements promote various reactions/interactions in humic samples. For example, glycerol, due to the three potential reaction sites, could cause chaining of humic 'clusters' and thus protect them against thermo-oxidative degradation. This conclusion is supported also by the total mass loss that is in comparison with the HA as well as HA1-10 and HA2-10 significantly lower.

Addition of alkanes

After the addition of alkanes in any concentration to the original HA, the temperature of onsets slightly decreased. Maximum of the first peak was shifted to higher temperature for the 10% samples whereas it slightly decreased for the 1% additons. Cyclohexane-treated sample HA5-10 degraded in one step resulting in the intense exothermic peak. TGI was slightly lower which is in line with previous presumptions. The decrease of stability of treated samples was

Table 2 Parameters obtained from simultaneous DTA and TG records for 10% enriched samples. T_o is the onset temperature of degradation, T_1 and T_2 stand for the peak temperatures of the first and second degradation step, respectively. TGI was calculated as the ratio of mass losses in temperature regions corresponding to second (C), third (D) and first degradation steps (B)

Sample	Abbrev.	Sample mass/mg	DTA/°C			TG–mass loss/%				Total loss/%	TGI index
			onset	T_1	T_2	A	B	C	D		
pure HA	HA	1.78	238.9	415.9	470.8	8.9	43.8	32.6	2.6	87.9	0.80
Alcohols											
ethanol	HA1-10	1.89	236.9	417.3	458.7	5.0	56.5	22.4	5.8	89.7	0.50
octanol	HA2-10	1.74	237.0	412.7	456.4	8.9	60.8	12.7	9.3	91.7	0.36
glycerol	HA3-10	2.00	248.5	415.0	470.6	5.9	42.8	28.6	5.4	82.7	0.79
Alkanes											
heptane	HA4-10	2.16	234.2	417.9	465.3	7.2	44.1	25.1	2.7	79.1	0.63
cyclohexane	HA5-10	1.94	231.3	421.3	–	7.9	53.8	34.7	34.7	96.4	0.65
Ketone											
cyclohexanone	HA6-10	1.67	238.4	407.0	471.1	9.9	40.2	30.5	6.5	87.1	0.92
Organic acids											
formic acid	HA7-10	1.86	237.9	410.7	450.5	5.2	59.8	10.1	11.5	86.6	0.36
acetic acid	HA8-10	1.88	246.8	411.2	478.5	8.1	39.5	34.0	5.3	86.9	1.00
propionic acid	HA9-10	1.59	234.5	422.7	–	9.6	51.7	25.0	25.0	86.3	0.48
palmitic acid	HA10-10	1.96	244.9	409.7	471.3	12.0	42.6	32.4	4.9	91.9	0.88
benzoic acid	HA11-11	1.85	234.6	409.5	460.0	4.3	59.3	11.0	11.0	85.6	0.37
Aromatic compounds											
phenol	HA12-10	1.83	234.4	422.3	–	7.2	51.5	29.9	29.9	88.6	0.58
benzene	HA13-10	1.82	233.7	419.3	–	7.1	54.3	34.6	34.6	96.0	0.64
benzoyl peroxide	HA14-10	1.77	237.7	410.3	463.7	3.5	51.0	16.3	12.5	83.3	0.57
p-xylene	HA15-10	1.79	242.0	410.8	477.7	6.0	38.3	44.1	4.0	92.4	1.26
p-cresol	HA16-10	1.97	242.0	412.3	475.8	4.9	27.1	44.7	4.0	80.7	1.80
m-cresol	HA17-10	1.74	236.8	408.2	468.4	8.6	39.9	25.6	11.0	85.1	0.92
pyrocatechol	HA18-10	1.76	244.2	411.9	474.5	8.3	40.1	33.5	2.4	84.3	0.90
hydroquinone	HA19-10	1.90	242.5	406.7	470.7	6.9	40.3	27.5	11.7	86.4	0.97
Heterocyclic compound											
pyridine	HA20-10	1.94	222.3	420.1	469.0	8.8	52.8	26.1	5.3	93.0	0.59
Sterole compound											
cholesterol	HA21-10	1.99	236.8	418.0	466.4	7.3	52.9	23.0	5.5	88.7	0.54

expected because it is known that aliphatic parts of HA degrade in the first step. In fact, the added alkane compounds were not completely dissolved in the HA samples. Although HA are known to support solubilization of hydrophobic compounds due to their amphiphilic nature, 10% of hydrophobic substance is far behind their solubilization capacity. Likely no reactions leading to formation of new bonds occurred, but the difference between the samples under investigation is significant. Using excess of methanol to change conformation arrangement in sodium humate, the opposite effect has been observed in [17]. The result was explained by the separation of hydrophobic and hydrophilic parts (domains), where the former were more tightly bound together because of the phenomenon known as the 'hydrophobic effect' that consequently increased the thermal stability [17, 18]. In this work the pH value of HA samples used in preparation was around 4.2 and therefore partial protonization of carboxylic groups can be expected. Those are less stable and after separation of the domains they show lower thermal stability.

Addition of ketone

Addition of cyclohexanone (HA6-10) decreased T_o only in case of the 1% addition. TGI was in both cases higher. It indicates that cyclohexanone is not degraded in the first step and possibly plays a role in formation of new (aromatic) structures. Referring to the sample HA6-10, the mass loss in the region D, that is attributable to the degradation of mainly polyheterocyclic parts, significantly increased. Explanation may be seen in the presence of the reactive group that can be (in contrast to cyclohexane) involved in new chemical bonds formation.

Addition of organic acids

Addition of organic acids into HA sample showed no clear correlation between concentration and nature of the acid and TA parameters (Tables 1 and 2). Formic acid (HA7-1 and HA7-10) addition caused a slight increase of T_o in both cases whereas TGI decreased for the 10% addition significantly and the opposite change was observed for the 1% sample.

Sample treated by the 1% acetic acid (HA8-1) showed decrease of the onset temperature and slight increase of TGI. On the contrary, 10% of acetic acid increased the T_o as well as TGI.

In the case of 10% propionic acid sample (HA9-10), the degradation proceeded in one intense exothermic step with a down-shift of T_o. T_o of the HA9-1 sample increased, TGI decreased.

The exception can be seen in the case of palmitic acid (HA10-1 and HA10-10) where an increase of T_o as well as of TGI can be seen. Possibly, a part of palmitic acid evaporated (the region A) due to the low solubility in water.

Addition of benzoic acid at the low concentration (HA11-1) caused the increase of both T_o and TGI and at the higher concentration their decrease.

The influence of organic acids on the molecular arrangement of HA has been described in [9]. Due to the amphiphilic structure (of acetic and propionic acids in our case), they cause disruption and reaggregation of the hydrophobic domains. Moreover, the decrease of pH supports protonization of carboxylic groups in the HA molecules which increases the importance of H-bonds. The latter cannot be expected in the case of palmitic acid; the increase in stability can be better ascribed to the 'hydrophobic effect' which is caused by approaching of hydrophobic parts closer to each other [17, 18].

It can be seen that there is no clear relation between the chemical character of added molecules and parameters of thermo-oxidative degradation. The TGIs indicate that various amounts of added organic acid can play an important role in the recombination processes during the thermo-oxidative treatment.

Addition of aromatic compounds

As it has been mentioned previously, hydrophobic compounds in such amount as used in this work cannot be dissolved. On the other hand, mass loss of the treated samples recorded in the A region was lower or comparable with the original HA; therefore it can be assumed that those compounds were not completely evaporated and took part in the degradation processes. T_o was higher for *p*-xylene and hydroquinone (HA15-1, HA15-10 and HA19-1, HA19-10, respectively).

A decrease of both parameters was recorded for the samples with benzene addition (HA13-1 and HA13-10). Similar data were obtained for *m*-cresol samples (HA17-1 and HA17-10), though their TGI slightly increased, and for phenol samples (HA12-1 and HA12-10) where TGI of the 1% sample slightly increased. On the other hand, *p*-cresol samples (HA16-1 and HA16-10) resulted in a higher TGI for both concentrations, in a decrease of T_o for the 1% and increase for the 10% samples. The same shifts were observed also for the hydrochinon-treated samples (HA18-1 and HA18-10) whereas for the benzoyl peroxide samples (HA14-1 and HA14-10) the trend was opposite.

TGI reflects the role of added molecules during the recombination processes resulting in new polyaromatic moieties formation. The most significant change is seen for HA16-10, its TGI is more than two times higher than for the original HA. To summarize the findings, there is no general dependence of higher stability for the samples rich in aromatic moieties content. Likely, the selected model compounds belong to both groups of aromatic molecules, non- and humified. Remarkable, however, is the different effect of addition of *para*- and *meta*-cresols.

Addition of heterocyclic compounds

Addition of pyridine (HA20-1 and HA20-10) significantly decreased T_o as well as TGI. Therefore, it can be assumed that pyridine is decomposed in the first step and does not play any role in the recombination reactions leading to the formation of new aromatic structures. It is likely that, due to the low polarity of the nitrogen atom in pyridine structure, pyridine was only trapped or adsorbed in the humic acids. This assumption is supported by the mass loss in the temperature region A, that is almost equal to the original HA sample; hence, it seems to correspond only to the moisture evaporation.

Addition of sterol compound

The addition of cholesterol, which belongs to the chemical group of lipids, samples HA21-1 and HA21-10, shifted T_o of the former sample to higher temperatures and of the latter one to lower temperatures. On the other hand, TGI significantly decreased. That observation is in agreement with the fact that non-humified compounds degrade or recombine in the first step of TA treatment.

Conclusions

Simultaneous DTA and TG records have been used to study the influence of model compounds such as

aromatics, organic acids, alkanes, alcohols, heterocyclic and sterol molecules on the thermooxidation of lignite humic acids. As a measure of stability, the changes of onset temperature of the exothermic degradation peak has been used. Ratio of mass loss recorded in the high and low temperature ranges (thermogravimetric index) was used for evaluation of the influence of the added compounds on the recombination reactions occurring during the thermooxidative degradation of humic acids. It has been demonstrated that most of added compounds affect the stability of humic acids at relatively low concentrations. The changes of thermogravimetric index (i.e., the degree of the apparent aromaticity) show that its value can be significantly biased by the presence of small amount of some compounds. Thus, it has been clearly shown, that such a parameter reflects more the 'qualitative' than the 'quantitative' relationship between biodegradable a humified parts.

Acknowledgements

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