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INVESTIGATION OF SUBBITUMINOUS COALS BY THERMOGRAVIMETRY–MASS SPECTROMETRY. PART 1. FORMATION OF HYDROCARBON PRODUCTS

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ABSTRACT

The thermal decomposition of a series of subbituminous coals from a Hungarian coal basin was investigated by thermogravimetry–mass spectrometry at a heating rate of 20 °C min^{-1}. The mass spectrometric intensities of the aliphatic products (C_nH_m, $n \geq 2$) and alkyl-substituted aromatic compounds evidenced similar sharp peaks at about 490 °C. Methane evolved at higher temperatures in a broader temperature range. Benzene curves were composed of two overlapping peaks and were resolved by least-squares reaction kinetic calculations. The low and high temperature peaks of the benzene curves were near to the peaks of the aliphatic C_nH_m ($n \geq 2$) compounds and methane respectively. The amounts of the various products were estimated by the integral of the corresponding mass spectrometric intensities and were correlated with coal rank. The probable sources of the various product compounds were discussed.

INTRODUCTION

Thermogravimetry–mass spectrometry (TG–MS) has proved to be a useful technique for the characterisation of coals [1–7]. This technique simultaneously provides quantitative data as functions of temperature about the mass loss of the sample and the evolution of the decomposition products.

In this study a series of subbituminous coals from a Hungarian coal basin (Nógrád) was investigated by TG–MS. Our aim was to contribute to the deeper understanding of the thermal decomposition process. A particular emphasis was placed on elucidating the most probable source structures in the coals of the various decomposition products. The evolution of the oxygen- and sulphur-containing products and the kinetics of the overall mass loss during the decomposition are treated in Part 2 of the paper [8]. Some preliminary results about the thermal decomposition of the same series of coals were presented earlier [9]. The extracts of the coals were extensively studied by Alexander et al. [10] and Grimalt et al. [11].

EXPERIMENTAL

Apparatus and experimental conditions

A Perkin–Elmer TGS-2/System 4 thermobalance was coupled to a Balzers QMG 511 mass spectrometer and provided with computerised data acquisition and data processing equipment [12,13]. A cross-beam ion source, electron energy of 70 eV and an electron multiplier were applied. Small amounts of samples (ca. 8 mg) were heated from 20 ° C to 950 ° C at a slow heating rate (20 ° C min^{-1}) in an open platinum crucible. The ambient gas was high purity dry argon with a gas flow rate of 180 ml min^{-1}. Part of the carrier gas was introduced into the mass spectrometer through a heated silica capillary which connected the thermobalance to the ion source. Mass spectrometric intensities up to $m/z = 182$ were measured as functions of temperature. (The highest background peaks of the argon carrier gas, $m/z = 20$, 36 and 40, were bypassed in the scans.) After subtracting the background level and making some corrections for a few well-defined fragmentation patterns, the intensities were normalized with the initial sample mass and the intensity of ^{38}Ar. (The stable ^{38}Ar concentration was used as an internal standard to eliminate the variation of the mass spectrometer sensitivity between the experiments.) Ion curves close to the noise level were omitted. The mathematical criterion for the rejection was a signal/noise ratio of less than 10. The DTG curves were calculated numerically. As well as in coal researches, the apparatus and experimental procedure have proved useful in the characterisation of biomass materials [13–15].

Limitations of the applied experimental procedure

The factors limiting the possibilities of deduction in this study are listed here as follows.

(i) The tar fraction (compounds having boiling points higher than 180 ° C) is not detected by the mass spectrometer.

(ii) Most mass spectrometric fragments are formed from more than one compound. Thus the interpretation is based partly on the intensities of simple fragments of well-defined origin ($m/z = 18$, 28, 44, 64), and partly on fragments characteristic of certain groups of decomposition products.

(iii) Quantitative calibrations could be carried out only for the evolution of H_2O, CO and CO_2. The actual amounts of the products contributing to the other mass spectrometric intensities are not known exactly. Therefore the mass spectrometric intensities are given in arbitrary units only. However, we can compare quantitatively the different values of the same mass spectrometric intensity within a given series of experiments.

(iv) Similarly to the other techniques of thermal decomposition studies, secondary reactions may arise between the product compounds [16].

TABLE 1

Characterisation of the coal samples

Sample	Ash (d, %)	Volatile matter (d, %)	Composition of the organic phase (daf, %)					Huminite reflectance R_m
			C	H	O	N	S	
M-1	44.6	22.3	75.4	5.2	18.6	1.4	1.2	0.63
M-2	49.8	21.2	73.8	5.3	17.4	1.3	2.2	0.65
S	31.7	27.5	74.6	5.1	18.4	1.6	0.3	0.54
K-1	25.4	31.2	69.6	4.9	21.0	1.7	2.8	0.39
K-2	23.3	35.6	68.1	4.4	22.0	1.2	4.3	0.38

Samples

The properties of the samples are shown in Table 1. The coals were formed in the lower Miocene in a coastal swamp environment. The samples originated from three areas: Kányás (K-1 and K-2), Ménkes (M-1 and M-2) and Szorospatak (S). The coals of Ménkes and Szorospatak were influenced by thermal intrusions of nearby volcanos during their formation. More details about the diagenesis of the coals were given by Alexander et al. [10] and Grimalt et al. [11]. The rank of the coals is characterised by the maximum huminite reflectance, R_m, which is an analogous parameter to the maximum vitrinite reflectance of the higher rank coals. Establishing correlations between coal rank and product evolutions in this study, we obtained better correlations (less scattering) using R_m as a rank parameter than C_{daf} or C_{daf}/H_{daf}. The samples were pulverised and dried before the experiments.

RESULTS AND DISCUSSION

Figure 1 shows the DTG curves of three coal samples. The first peak, about 150 °C, is water desorption. The relatively slow mass loss of the

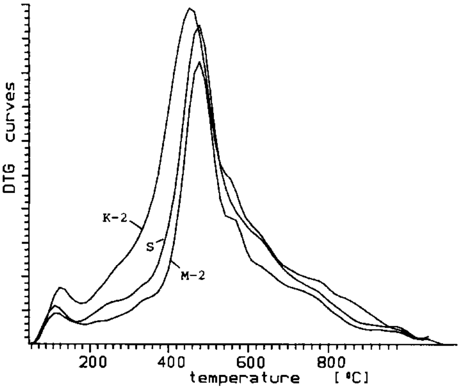

Fig. 1. DTG ($-dm/dt$) curves for coals K-2, S and M-2.

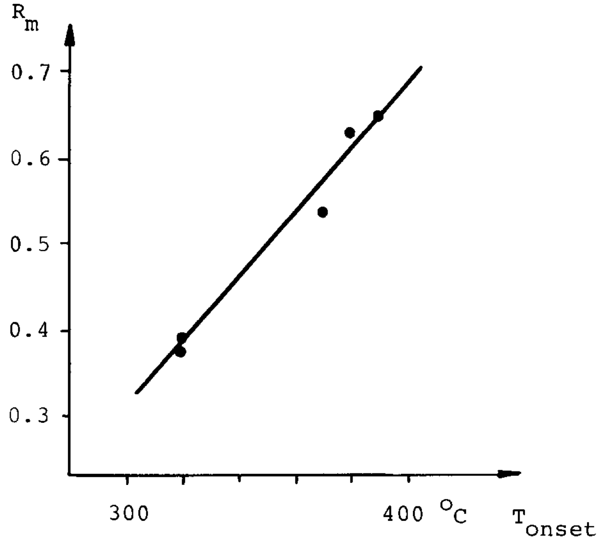

Fig. 2. Variation of the extrapolated onset temperature (T_{onset}) with huminite reflectance (R_m).

decomposing samples below 350 °C is dominated by water and carbon dioxide release. Below 400 °C the rate of the mass loss strongly depends on the rank of the coals. The most active part of the thermal decomposition takes place between 350 °C and 650 °C where most ion intensity curves exhibit maximum rates. The beginning of this region can be characterised by the extrapolated onset temperature, T_{onset}, defined as the point of intersection of the tangent drawn at the point of greatest slope on the leading edge of the DTG curve with the T axis [17]. T_{onset} was found to vary linearly with the coal rank, as illustrated in Fig. 2. In the high temperature domain of the decomposition (above 650 °C) there is no considerable mass loss. Here the coking of coal takes place, producing mainly CO and H_2 as well as the coke.

In the subsequent part of the paper we shall interpret mass spectrometric ions intensities characteristic of various groups of products.

Aromatic products

The relative amount of the formed volatile aromatic compounds, estimated roughly by the sum of their mass spectrometric intensities, proved to be considerably smaller than the amounts of other characteristic decomposition products (H_2O, CO, CO_2, H_2, CH_4, C_nH_m ($n \geq 2$) and sulphur-containing products). Figure 3 illustrates the corresponding magnitudes and temperature domains. The main observed aromatic products were benzene, naphthalene, indene, phenols, and their derivatives. The intensity curves attributed to benzene and its derivatives are shown in Fig. 4. It is interesting to note that the intensities belonging to alkyl-substituted benzene compounds

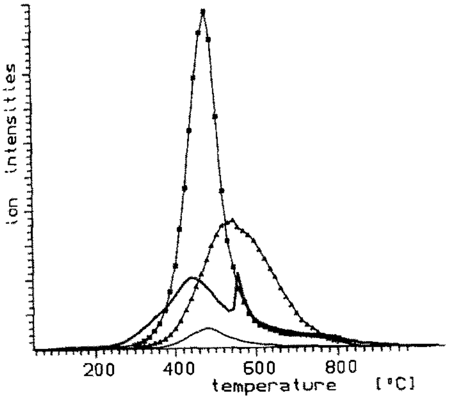

Fig. 3. Comparison of the approximate amounts and temperature domains of three different type of products of coal K-2: □———□, sum of C_nH_m fragments ($n \geq 2$); ———, sum of aromatic fragments; ———, sum of sulphur-containing fragments; △———△, methane ($m/z = 16$).

($m/z = 91$, 105, 119) and aliphatic hydrocarbons ($m/z = 26$, 27, 41, 43, 55, 57 etc.) had the same shapes and peak temperatures. (See Fig. 5. The small differences revealed in the high temperature region of Fig. 5 will be discussed later.) The coincidence of these two groups of compounds indicates that they are the results of the same chemical reaction: the thermal scission of the aliphatic bridges connecting the aromatic units to the coal matrix. On the other hand, the ion intensity curves of the benzene ($m/z = 78$) and naphthalenes ($m/z = 128$, not shown in the figures) were composed of two overlapping peaks. Here the second peaks, at about 600 °C, may belong to the scission of some heat-resistant bridge structures. The exact nature of these stronger bridges is unknown; they may be aromatic ether bonds as well

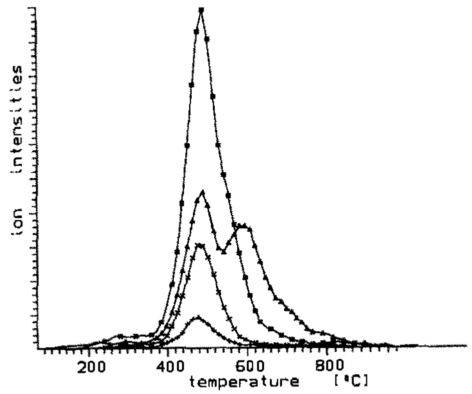

Fig. 4. Evolution of benzene and benzene derivatives from coal M-2: △———△, benzene ($m/z = 78$); □———□, toluene ($m/z = 91$); ×———×, xylenes ($m/z = 105$); +———+, trimethylbenzene ($m/z = 119$). (Arbitrary intensity units are used in the figures.)

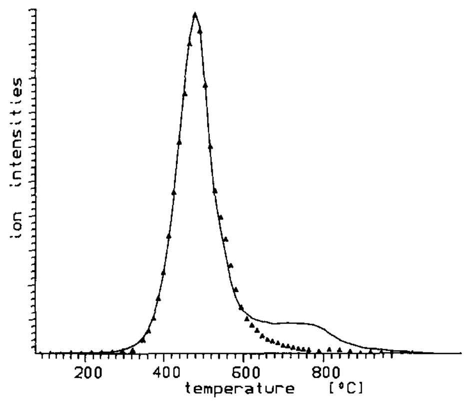

Fig. 5. Two selected ion intensities of coal K-2: ——, $m/z = 27$ ($C_2H_3^+$ and HCN); △, $m/z = 91$ (toluene).

as fluorene-type structures and heterocyclic units connecting benzene rings to the coal matrix. The amounts of the aromatic compounds increased with the coal rank as Fig. 6 shows.

Aliphatic products C_nH_m *(n ≥ 2)*

The light hydrocarbon products may be due to the decomposition of the linear paraffinic groups bound chemically to the polymeric structures or trapped in the microporous structures of coals, hydroaromatic units, aliphatic

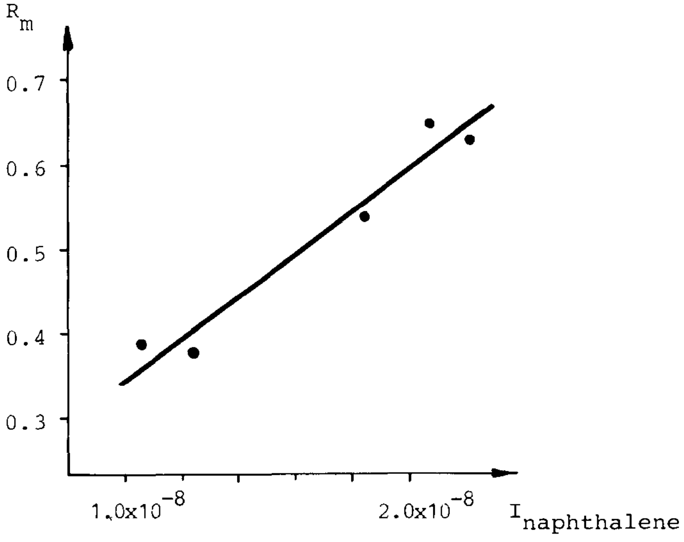

Fig. 6. Dependence of the amount of the evolved naphthalene on the coal rank. ($I_{naphthalene}$ denotes the integral of the intensity of the $m/z = 128$ peak calculated on a dry ash-free basis.)

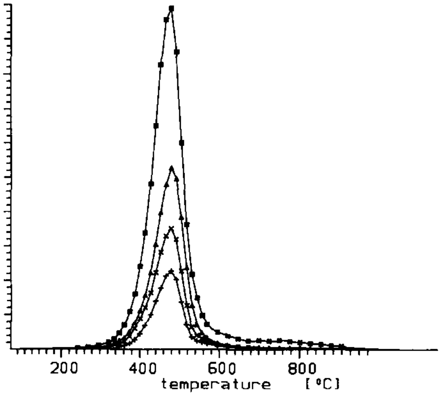

Fig. 7. Intensities of aliphatic hydrocarbon fragments of coal K-2: □——□, $C_3H_5^+$; △——△, $C_3H_6^+$; ×——×, $C_4H_7^+$; +——+, $C_4H_9^+$.

bridges and some oxygen-containing polymethylene compounds (*n*-fatty acids, *n*-alcohols, *n*-ethers, etc.) during the heating of the coals [18–20]. In our case the mass spectrometric fragments of these compounds evidenced sharp peaks with regular shapes and peak maxima around 490 °C (see Fig. 7). It is interesting to note that ion intensity $m/z = 27$ has a high temperature tail between 600 and 800 °C (see Fig. 5) which may be due to HCN evolution. Although our instrument did not allow experimental differentiation between $C_2H_7^+$ and HCN^+, it seems highly probable that the cracking and rearrangement of the nitrogen-containing heterocyclic aromatic structures of the coal produce HCN at higher temperatures.

Methane

Methane is the most important aliphatic pyrolysis product. It gives two identical mass spectrometric ions, $m/z = 15$ and 16. ($m/z = 16$ was corrected by subtraction of the O^+ intensities arising from H_2O, CO and CO_2.) Methane evolves at higher temperatures and in a wider domain than the other aliphatic products (see Fig. 3). The higher temperatures indicate that methane is evolved from different chemical reactions to the other alipathic hydrocarbons. This is in accordance with the conclusions of Ofosu-Asante et al. [21]. The wide temperature domain indicates that methane probably evolves from more than one source. It is interesting to note that the high temperature methane evolution and the second peak of the benzene production occur in the same temperature domain (see Fig. 8). It seems probable that these processes, from about 550 °C to 850 °C, are connected with the rupture, rearrangement and fusion of the various aromatic structures. The relatively high abundance of the formed methane among the decomposition products is related to the high thermal stability of this compound. A smaller proportion of methane is probably formed by secondary char autohydro-

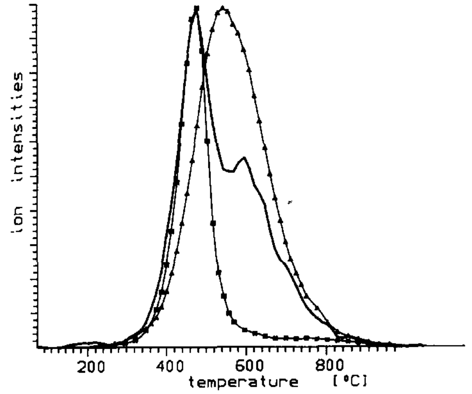

Fig. 8. Comparison of three ion intensities of coal K-2: △——△, methane ($m/z = 16$), □——□, $C_3H_5^+$; ——, benzene. (The curves are magnified to equal scale.)

genation ($C + 2H_2 \rightleftharpoons CH_4$). The assumption of the aromatic origin of a significant part of the methane evolved is also supported by the increase of the amount of methane with coal rank (see Fig. 9). Note that Fitzgerald and van Krevelen [22] studied the dependence of the amount of methane on the carbon content of the coals in a wide range of coal ranks and reported a maximum curve with a peak position at 89% (daf) carbon content. The maximum curve they reported may also be interpreted in such a way that a considerable part of the methane arises from the various aromatic structures of the coals. (The amount of the aromatic structures increases with coal

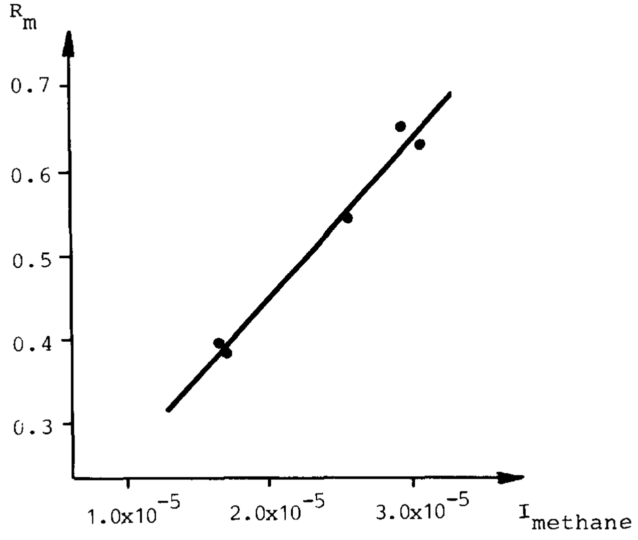

Fig. 9. Dependence of the amount of the formed methane on the coal rank. (I_{methane} denotes the integral of the intensity of the $m/z = 16$ peak calculated on a dry ash-free basis.)

rank. At high carbon content, however, this increase is counterbalanced by the overall decrease of the volatile matter.)

Hydrogen

Hydrogen evolved mainly in the final region of the decomposition of coal. The evolution of hydrogen seems to follow the fusion of the aromatic ring structures (lamellae) in the coal matrix. The temperature range belonging to the hydrogen MS ion curve is rather wide, indicating that the rate-determining step is probably the diffusion of two lamellae into configuration where reaction becomes possible [23].

Reaction kinetic considerations

The modelling of the whole system of chemical reactions producing volatile hydrocarbon compounds was beyond the scope of the present paper. We applied reaction kinetic evaluation only in the study of two relatively simple problems. The first one was connected with the work of Jüntgen and van Heek [24] who described the production of ethane from coals by a single first-order reaction and obtained reasonable A and E values (10^9 s^{-1} and 180 kJ mol^{-1}) in a wide range of heating rates. We observed similar, sharp peaks for the intensities characteristic of the aliphatic products (see Fig. 7). Fragments $C_3H_5^+$ and $C_3H_6^+$ appeared particularly well suited for reaction kinetic evaluation since they did not have the high temperature tail observed by Jüntgen and van Heek [24] at $m/z = 26$ and they revealed slightly asymmetric shapes characteristic of first-order reactions [25]. The second problem was the clarification of the double peak of the benzene evolution. We resolved the overlapping peaks by using the combination of two independent first-order reactions:

$$d\alpha/dt = c_1\, d\alpha_1/dt + c_2\, d\alpha_2/dt \tag{1}$$

$$d\alpha_i/dt = A_i \exp(-E_i/RT)\,(1-\alpha_i) \qquad (i = 1, 2) \tag{2}$$

where α, α_1 and α_2 are reacted-fraction-type quantities (varying from 0 to 1) describing the overall production of benzene and its evolution from the first and second partial reactions respectively. c_1 and c_2 denote the relative amounts of benzene formed in reactions 1 and 2 respectively. The measured data were approximated by their theoretical counterparts by the method of least squares. The algorithm was published previously [25]. Acceptable fits (deviations comparable with the experimental uncertainty) were obtained in all cases. The kinetic constants (A and E) belonging to $C_3H_5^+$ and $C_3H_6^+$ were approximately identical. There was a variation between the coal samples. Coals K-1 and K-2 have exhibited the lowest values ($A \approx 10^7$ s^{-1} and $E \approx 126$ kJ mol^{-1}) while the evaluation of coal S resulted in the highest

E and A, 10^9 s^{-1} and 160 kJ mol^{-1} respectively. Although the latter values may be accepted as real unimolecular parameters, it is more probable that the assumption of a single first-order reaction is only a formal approximation of a more complex radical decomposition scheme. Nevertheless, formal approximations may be useful in the numerical characterisation of experimental curves as well as in the resolution of double peaks. The A and E values of the low temperature peak of benzene evolution were approximately equal to the corresponding values of the aliphatic peaks of the same coal samples, emphasising the common origin of the aliphatic products and benzene at about 500 °C. The parameters of the high temperature benzene peaks were extremely low. This may be due to the broad shape of these peaks and indicates that benzene is produced by several different types of reactions above 550 °C. The obtained values of c_1 and c_2 indicate that about 65–75% of the benzene is formed in the high temperature reactions.

CONCLUSIONS

In Part 1 of the paper the evolution of the volatile hydrocarbon products was studied. Mass spectrometric ion intensities were measured as functions of temperature. The main conclusions are as follows.

(i) The intensity curves of the aliphatic products (C_nH_m, $n \geq 2$) showed well-defined sharp peaks with shapes resembling those of first-order reactions. The corresponding reaction kinetic parameters, however, were slightly lower than the values belonging to true unimolecular reactions.

(ii) The similarity of the intensity curves of the aliphatic products and the aromatic products with aliphatic side groups suggests that these two groups of compounds are generated by the same chemical reactions.

(iii) Benzene and naphthalene evidenced characteristic double peaks. The numerical resolution of these peaks showed that about one-third of the overall benzene production occurred in the low temperature region, at temperatures identical to those of the aliphatic products. We can assume that the two partial peaks belong to different types of bridge structures connecting benzene rings to the coal matrix: aliphatic bridges in the low temperature region and partly aromatic and heterocyclic structures in the high temperature region.

(iv) Methane evolved at higher temperatures than the other aliphatic products. Since the peak temperatures of the methane curves were near to those of the second benzene peaks and the overall amount of the evolved methane increased with coal rank, we can assume that a considerable part of the methane is formed from aromatic structures.

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