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STUDIES OF THERMAL TRANSFORMATION OF HUMIC AND FULVIC ACIDS IN SOILS II. THERMOGRAVIMETRY

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The thermogravimetry and differential curves of the humic and fulvic acids in the soils from five areas of China were determined and the peaks of these curves were classified according to the results of infra-red (IR) spectra at high temperature and pyrolysis-mass spectra (Py/Ms). The kinetic parameters for heat-degradation of these humic and fulvic acids were calculated by the Coast-Redfern method. The initial temperatures, the final temperatures, and the peaks of DTG curves, the activation energies, the reaction orders and the percentages of weight loss at different reaction stages for these samples were analysed. Thus, the similarity of thermal transformation of humic and fulvic acids in the soils from different areas of China was demonstrated. In addition, the DTA curves of red earth HA and FA were determined.

Keywords: Humic acid (HA); fulvic acid (FA); kinetics; thermal transformation; thermal gravimetry

INTRODUCTION

Thermogravimetric analysis combined with infra-red spectrometric and mass spectrometric analyses is a powerful tool for studying the thermal transformation pathways of humic and fulvic acids in soil, because both spectrometric techniques improve the basis for the interpretation of the

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thermogravimetric (TG) and the differential thermogravimetric (DTG) curves, as well as differential thermal analysis (DTA) curves.

The purpose of this paper is threefold: (a) to determine the TG and DTG curves of five humic acids and five fulvic acids from different soils; (b) to assign the peaks of these DTG curves; (c) to determine the activation energies and specific rate constants for the main decomposition reaction steps of these humic and fulvic acids. The combination of TG and DTG curves with IR and Py/Ms spectra would provide the additional information on the "inside" of these humic and fulvic acids.

EXPERIMENTAL SECTION

Materials

Origins, elemental composition, moisture and ash contents of five humic acids and five fulvic acids were described in the previous paper (Tao Zuyi *et al.*, 1997).

APPARATUS AND EXPERIMENTAL METHOD

The sample size ranged from 3 to 14 mg. The samples were heated from room temperature to 850°C under nitrogen on a Dupont 1090 W model thermal analysis apparatus which allows simultaneous recording of TG and DTG curves.

The DTA curves were obtained with the same apparatus and at the same conditions.

RESULTS AND DISCUSSION

1. Thermogravimetric and Differential Thermogravimetric Curves

Thermogravimetric (TG) and the corresponding differential thermogravimetric (DTG) curves for samples A to J are shown in Figure 1. A satisfactory interpretation of these curves is not possible because the decomposition reactions are not sufficiently separated. However, these DTG curves give considerably more information about the various

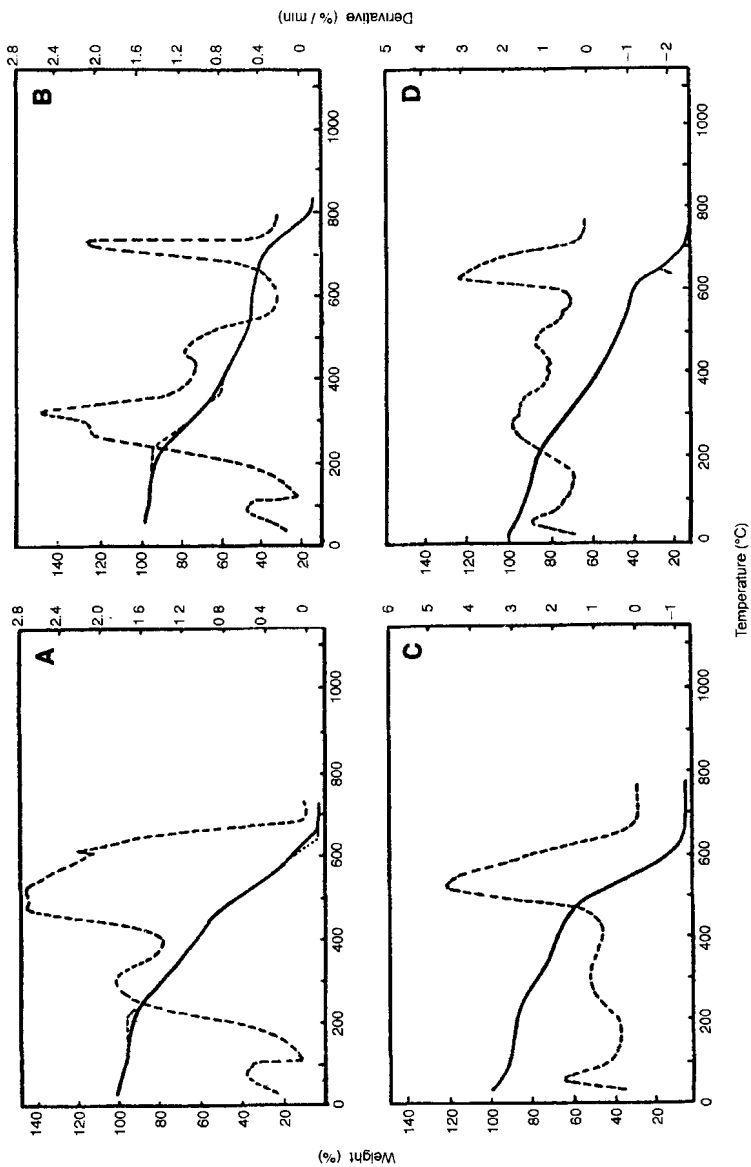


FIGURE 1 The TG and DTG curves of the ten samples A, B, C, D, E, F, G, H, I and J.

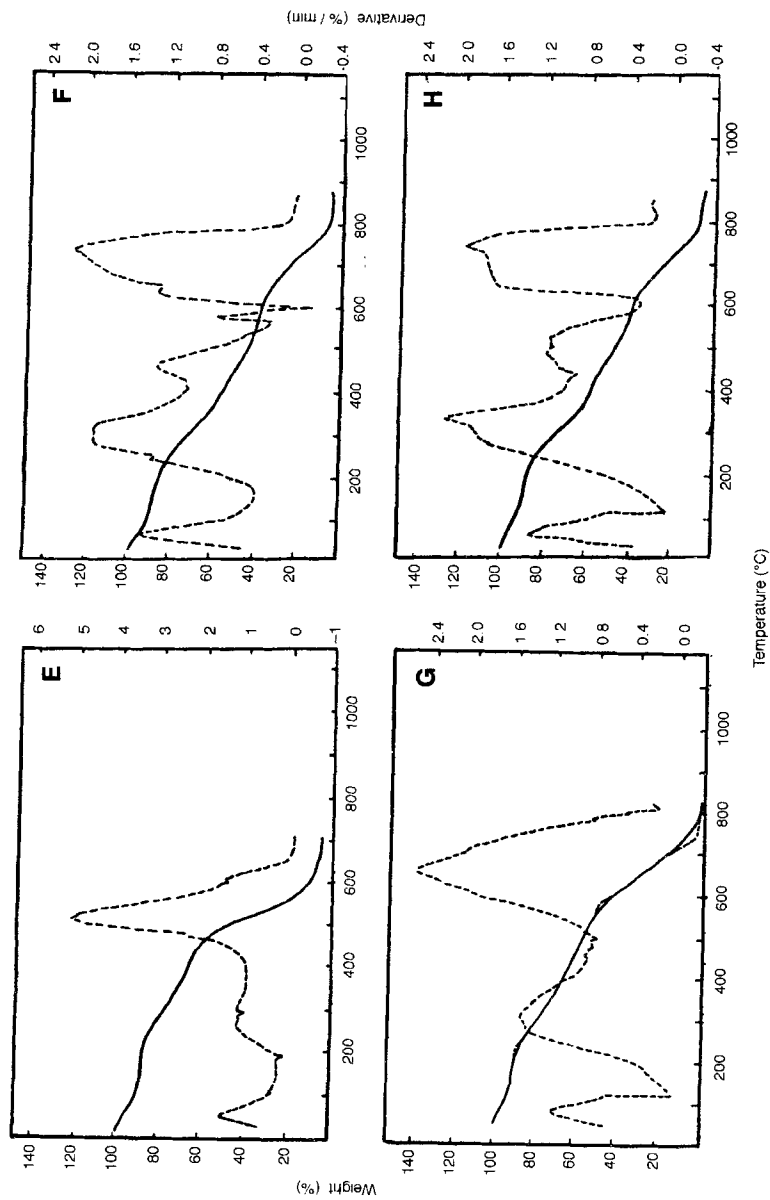


FIGURE 1 (Continued).

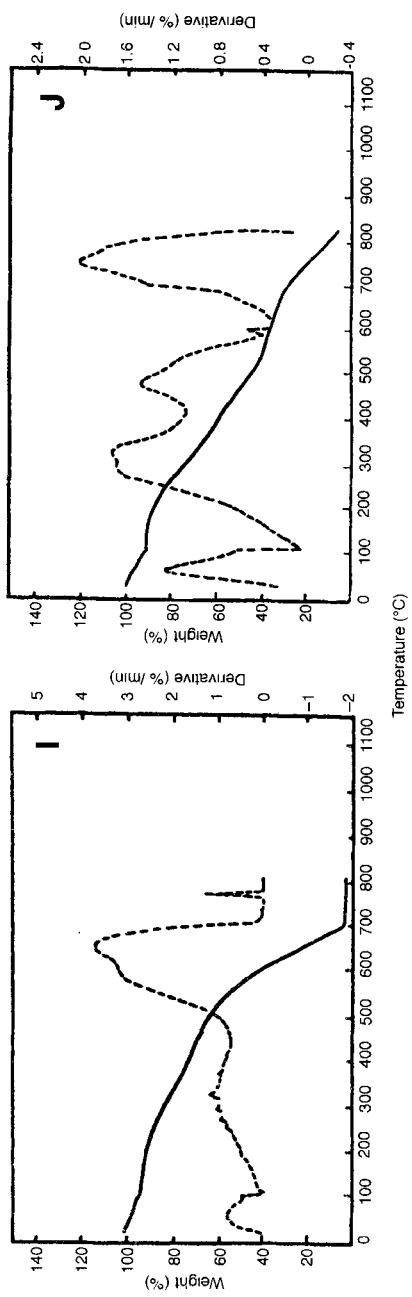


FIGURE 1 (Continued).

decomposition reactions than that of TG curves. All the further discussion in this paper will deal with DTG curves exclusively. The DTG curves for all HAs (samples A, C, E, G and I) exhibit three peaks in 50–100°C, 120–490°C and 400–780°C regions. The DTG curves for all FAs (samples B, D, F, H, J) exhibit four peaks in 50–100°C, 110–450°C, 410–600°C and 580–820°C regions.

The DTA curves for the samples A, B, G, H, I, J are shown in Figure 2. The DTA curves for all HAs are similar to each other and exhibit one shallow endothermic trough at about 95°C, one exothermic shoulder at about 320°C and one strong exothermic peak at about 470 ~ 640°C. The DTA curves for all FAs are similar to each other and exhibit one shallow endothermic trough at about 95°C, two

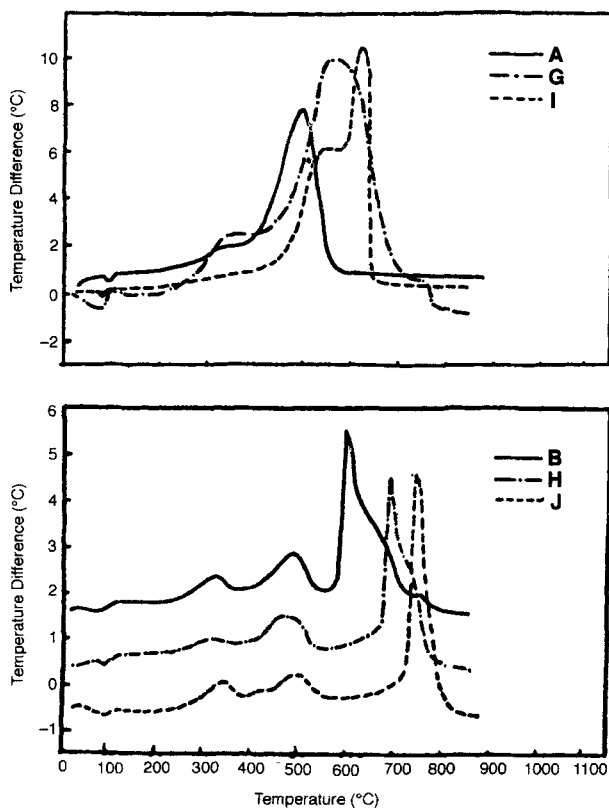


FIGURE 2 The DTA curves of the samples A, B, G, H, I and J.

small exothermic peaks at about 320°C and 470°C and one strong exothermic peak at about 720°C. The DTA curves are consistent with the DTG curves for HAs and FAs. The results demonstrate that the thermal transformations of HAs include three stages and that of FAs include four stages.

2. Assignments of the Peaks of DTG Curves

On the basis of previous IR and Py/Ms experiments on these HAs and FAs (Tao Zuyi *et al.*, 1997), the peaks in the DTG curves may be interpreted as follows: (a) the first peaks in 50–100°C temperature region are due to elimination of moisture for all HAs and FAs; (b) the second peaks in the 120–490°C region for HAs and the second and third peaks in the 110–450°C for FAs are chiefly attributed to decarboxylation and dehydration and (c) the third peaks in the 400–780°C region for HAs and the third peaks in the 410–600°C region for FAs are mainly attributed to the decomposition of condensed aromatic nucleus. Further, (d) the fourth peaks for FAs may be explained by a higher ash content in FAs and the formation of appreciable amounts of thermostable organo-mineral compounds, and these compounds are decomposed at a higher temperature. The data of weight loss (W%) at second stage for all samples are close to each other. The data of weight loss at the third stage for HAs range from 61 to 74, and these at the third stage for FAs range from 21 to 26, the average weight loss at third stage for HAs is greater than that of FAs. The difference of weight losses for HAs and FAs can be explained by the decompositions of condensed aromatic nucleus and of organo-mineral compounds for FAs which cannot be separated sufficiently.

The initial temperature (T_i , °C), the final temperature (T_e , °C) and the percentage of weight loss (W%) of various stages for HAs and FAs are respectively shown in Table I.

3. Kinetic Parameters of the Various Decomposition Stages

We believe that our results of section 2 provide the fundamental information on the decomposition mechanism of these HAs and FAs. Based on the results of section 2, the kinetic parameters of the various stages can be calculated from the TG curves by the Coats-Redfern integral method (Coats and Redfern, 1964). Though the use of thermogravimetric data to

TABLE I The TG data of HAs and FAs

No.	Stage 2			Stage 3			Stage 4		
	T_o	T_e	W^o_o	T_o	T_e	W^o_o	T_o	T_e	W^o_o
A	120	400	32.8	400	700	67.2			
B	110	420	39.0	420	580	21.0	580	800	40.0
C	160	400	28.8	400	670	71.2			
D	150	450	37.2	450	580	23.3	580	720	39.5
E	150	410	33.3	410	680	66.7			
F	160	430	32.9	430	590	24.5	590	790	42.6
G	120	490	38.5	490	780	61.5			
H	110	430	39.2	430	600	22.2	600	800	38.6
I	120	450	26.0	450	705	74.0			
J	110	410	39.2	410	600	26.9	600	820	33.9

evaluate kinetic parameters of solid-state reactions involving weight loss has been investigated by a number of researches (Turner and Schnitzer, 1962, Dubey *et al.*, 1993), a prior knowledge of the value of the reaction order of reaction was not assumed in the Coats-Redfern method.

The plots of $\text{Log}[(1 - (1 - \alpha)^{1-n})/(T^2(1 - n))]$ against T^{-1} of all samples for the different temperature ranges over which the different stages occur are not presented here but where α = fraction of reaction decomposed at time t , n = order of reaction, the order is given above.

On the assumption that the reaction order is constant throughout the reaction, the values of n were obtained by giving the best straight line through the experimental point. The kinetic parameters were calculated from the slopes and intercepts of straight lines of $\text{Log}[(1 - (1 - \alpha)^{1-n})/(T^2(1 - n))]$ against T^{-1} and are listed in Table II.

As shown in Table II, the reaction orders of the second stage are greater than those of the third stage, all the values of order of reaction are not equal to 1, all the reaction orders of second stage are higher than 1 and all the reaction orders of fourth stages are less than 1. From Table II, the activation energies of the second stages for HAs and FAs are close to each other and range from 4.9 to $6.2 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$, the activation energies of the third stage for HAs and FAs are also close to each other and range from 8.0 to $11 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$, the activation energies of the third stage are higher than those of the second stage for all HAs and FAs. The fourth stage for FAs exhibit the highest values of activation energy and are in excess of $11 \times 10^4 \text{ J} \cdot \text{mol}^{-1}$. As compared with the activation energies of third stages for all FAs, the

TABLE II The TG kinetic parameters at heat-degradation stage of all HAs and FAs in this experiment

Sample Stage	<i>n</i>	$E(\times 10^{-4})$ ($J \cdot mol^{-1}$)		k (s^{-1})	$A(\times 10^{-4})$ (s^{-1})	γ
A	2	2.10	6.08	0.220	8.62	0.9199
	3	1.80	9.10	0.210	12.9	0.9477
B	2	1.50	6.18	0.231	8.80	0.9070
	3	1.50	8.00	0.260	11.4	0.9189
	4	0.1	13.9	0.050	19.0	0.9647
C	2	2.1	6.12	0.395	8.74	0.8939
	3	0.9	9.45	0.165	13.3	0.9030
D	2	2.1	6.05	0.397	8.63	0.9549
	3	0.6	8.87	0.148	12.5	0.8944
	4	0.1	12.4	0.089	17.0	0.9437
E	2	3.0	5.98	0.749	8.63	0.9010
	3	0.3	9.26	0.133	13.0	0.9110
F	2	1.7	6.05	0.463	8.68	0.9819
	3	1.1	8.25	0.196	11.7	0.9740
	4	0.7	11.6	0.094	16.3	0.9250
G	2	3.0	5.51	1.110	8.82	0.5050
	3	1.6	10.6	0.177	14.8	0.9480
H	2	2.7	6.04	0.338	8.61	0.9896
	3	0.9	8.79	0.222	12.4	0.9479
	4	0.5	11.9	0.095	16.6	0.9110
I	2	3.0	4.87	5.55	7.33	0.9789
	3	1.4	10.3	0.159	14.4	0.9709
J	2	1.9	6.01	0.450	8.62	0.9369
	3	1.1	8.86	0.175	12.5	0.9060
	4	0.1	13.3	0.037	18.3	0.5970

note:

n: the reaction order, *E*: the activation energy ($J \cdot mol^{-1}$); *A*: the exponential factor (s^{-1}); *k*: the rate constant; γ : the regression coefficient

activation energies of the third stages for all HAs are higher; this difference can be attributed to the fact that the third stages for all HAs include the decomposition of organo-mineral compounds.

In our opinion, our results in this paper and the previous paper can give an insight into the chemical structures and reaction mechanisms controlling the degradation of humic and fulvic acids in soils.

CONCLUSION

Although the five HAs and five FAs were extracted from different areas of China and different climatic zones, all the samples show

similar thermal transformation pathways. The peaks of the DTG curves for HAs and FAs can be definitely assigned by combining thermal analysis with IR spectrometric and mass spectrometric analyses. The kinetic parameters including the activation energy and the reaction order can be obtained by using the Coast-Redfern method.

Acknowledgement

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