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Short Communication

SOME OBSERVATIONS ON THE THERMAL BEHAVIOUR OF CURCUMIN UNDER AIR AND ARGON ATMOSPHERES

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The TG, DTG and DTA curves of curcumin(I) have been recorded in static air and inert dynamic argon atmosphere over the range between ambient temperature and 600°–700°C using a Netzsch thermal analyser STA 429. Careful examination of these curves reveals appreciable differences in the behaviour of I under either atmospheres, which are easily recognized by comparing the profiles of their thermal curves, particularly in the melting point, thermal stability of intermediates, percent weight loss and exothermicity of the chemical processes. Gas-chromatographic analysis of volatile pyrolysates trapped during thermal analysis indicates the formation of $(CH_3)_2CO$, CH_3COH and $C_6H_5OCH_2COOH$ (phenyl oxyacetic acid). However, in static air CO_2 and H_2O were identified as well. X-ray diffractometry reveals the formation of amorphous carbon as a final product in argon and a mixture of amorphous carbon and graphite in air. It seems that the relatively high mass of argon plays an important role in the reactions and stability of intermediates. In either atmospheres curcumin is thermally stable up to 249°C with *m.p.* of 176.4°–177.5°C. The unique shape of the DTA curve of I could be used for its identification.

Keywords: curcumin, gas-chromatographic analysis, TG-DTG-DTA

Introduction

Curcumin, 1,7-bis(4-hydroxy-3-methoxy-phenyl)-1,6-heptadiene-3,5-dione, turmeric yellow, scheme 1, is an orange crystalline compound (1) which is insoluble in water (2) but soluble in some organic solvents and finds many applications in food and dye industries and agriculture. The annual world consumption

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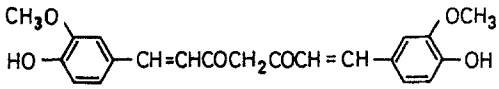
of this natural dye, which is obtained from the plant Curcuma Longa, is around 200000 tons.



It appears that no systematic thermoanalytical studies have so far been published on the behaviour of curcumin under air and argon. In this paper studies on the melting, thermal stability, volatility and intermediate and final decomposition products of I using simultaneous TG, DTG and DTA thermoanalytical techniques are described.

Table 1 Optimized instrumental parameters for the thermal degradation of curcumin

Parameters	Settings
Sample	Curcumin
Sample weight	40.00 mg
Reference material	Kaolin
Gas flow rate:	
Air	Static
Argon (10 $cm^3 \cdot min^{-1}$)	Dynamic
Crucible	Alumina
Heating rate	10 $deg \cdot min^{-1}$
Sampling time	3 s
Sensitivities:	
TG	25.00 mg
DTG	2.5 $mg \cdot min^{-1}$
DTA	50 μV

Experimental

Crystalline curcumin, from Fluka AG Buchs, was manually ground for 10 minutes in an agate mortar with a pestle. Thermal curves were recorded using a Netzsch STA 429 instrument. (Table 1). Volatile thermal degradation products were trapped and analysed by GC technique. Final solid products were identified by XRD.

Results and discussion

Figures 1 and 2 depict the TG, DTG and DTA curves of I under inert dynamic and static air, respectively. A mass loss of 1.09 wt% is due to the escape of a volatile impurity during the melting of the sample at 176.4°C. This weight loss, which is clearly indicated by the small endothermal peak on DTA curve ends at 249°C. Thereafter, the DTG curve exhibits the decomposition of I in two consecutive rather overlapped unequal steps. The first step, (249°–360°C), which is within the principal step (249°–448°C), DTG (ΔT_{min} = 400°C) represents the evolution (destructive distillation) of a molecule of acetone acetaldehyde and phenyl oxyacetic acid. The subsequent degradation of non-volatile intermediates resulted in the formation of amorphous carbon which is equivalent to 57.8 wt% of the sample weight near the maximum temperature of the heating program (around 635°C).

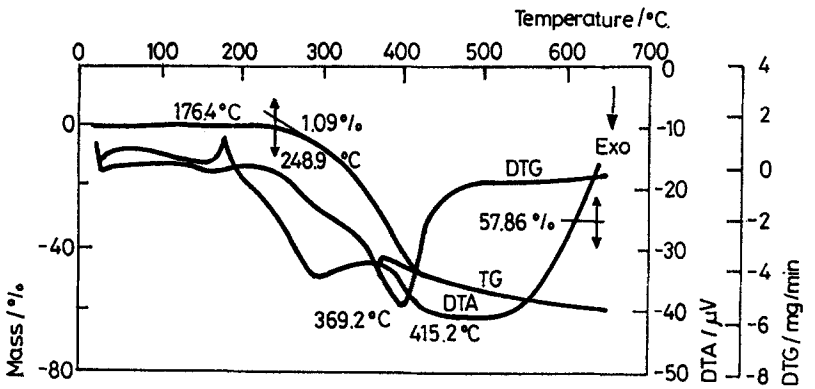


Fig. 1 TG, DTG and DTA curves of curcumin under argon atmosphere

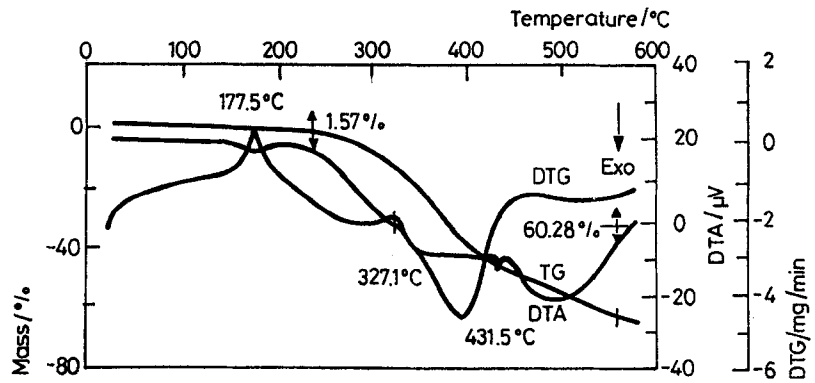


Fig. 2 TG, DTG and DTA curves of curcumin under air atmosphere

It is concluded that I is thermally stable in argon in the range from ambient temperature to 249°C. The segment of the TG curve between 249° and 415.2°C is rather steep; beyond it the slope gradually decreases. The TG curve may be used to derive the kinetic parameters of interest for curcumin degradation.

The sharp melting point endotherm ΔT_{min} = 176.4°C), (literature value = 175°–180°C), clearly seen on the DTA curve, indicates that appreciable destruction of I occurs only far beyond the melting point. The broad endotherm (ΔT_{min} = 369.2°C) indicates a slow degradation of non-volatile intermediates as heating proceeds. The absence of exotherms on the DTA curve (Fig. 1) excludes oxidation, combustion or crystallization processes. Incidentally, the disappearance of exotherms (compare 431.5°C, Fig. 2) infers the absence of changes in the crystalline graphite phase [3].

In air (Fig. 2) the weight loss due to volatile impurities is 1.57 wt% which accompanies the melting (ΔT_{min} = 177.5°C) of I. The first segment of the TG curve (249°–413°C) is less steep compared with the DTG curve taken in argon (Fig. 1). The final decomposition product constitutes 60.28 wt% of the sample. This 2.4% increase in the carbon content of the final product is attributed to the presence of air which enhances the combustion of sample. A distinguished feature of the DTA curve of I in air is the appearance of a small endothermal peak due to a change in the crystalline graphite phase (ΔT_{max} = 431.5°C); another feature is the lowering of the temperature of degradation of the second stage from ΔT_{min} = 369.2°C to ΔT_{min} = 327.1°C), Figs 1 and 2. Air oxygen not only promotes degradation but also increases its rate (the endothermal peak is sharp-er at ΔT_{min} = 327.1°C). It is worth noting that the net area of the endothermal peak at 327.1°C (Fig. 2) is smaller than that at 369.2°C (Fig. 1) due to thermal neutrality (decomposition-combustion reactions).

References

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2 Idem, 38 (1988) 106.
3 F. Jasim and I. Jameel, Thermochim. Acta, 147 (1989) 99.