Note

DERIVATOGRAPHIC STUDIES OF GALLIC ACID

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Thermal studies of gallic acid (3,4,5-trihydroxybenzoic acid) salts have been carried out by several workers [1—3], most of the studies were confined to pyrolysis of metal—gallic acid complexes. There seems to be no report on the pyrolysis of gallic acid from the analysis of TG, DTA and DTG curves. Hence, the thermal decomposition of gallic acid has been undertaken and a tentative scheme for the multistage decomposition is proposed. The thermogravimetric and isothermal studies enable us to arrive at conclusions which are supported by IR spectra.

EXPERIMENTAL

The gallic acid was of AR, BDH (England). Thermogravimetry (TG) was carried out using a Stanton-Redcroft thermobalance Model TG-770 and a Fisher differential thermalyzer Model 260P, fitted with an automatic voltage stabilizer, recorder and amplifier, was used for differential thermal analysis (DTA). About 10 mg samples were taken in platinum crucibles for TG and the heating rate was $10°C$ min^{-1}. Approximately 100 mg samples were taken for DTA in a quartz crucible using calcined α-alumina as reference material; the heating rate was $10°C$ min^{-1}.

Isothermal heating was carried out in a furnace fitted with a pyrometer and temperature controller. The accuracy of the temperature was $\pm5°C$. Infrared spectra were recorded with a Beckman IR-20 double beam instrument in the range $2000—250$ cm^{-1}, with samples in KBr pellets.

RESULTS AND DISCUSSION

Figure 1 gives the DTA, TG and DTG curves for gallic acid in air. The thermogram shows that dehydration of gallic acid starts at 333 K and is complete at 403 K, the maximum dehydration peak temperature being 358 K. The anhydrous salt decomposes in two stages, liberating 1 mole of carbon dioxide and 2 moles of water in the first stage between 493 and 563 K and another mole of water in the second stage between 568 and 633 K, and leaving carbon as residue which oxidizes completely between 653 and 993 K, showing almost 100% weight loss in TG. It can be seen that a 1 : 1 correla-
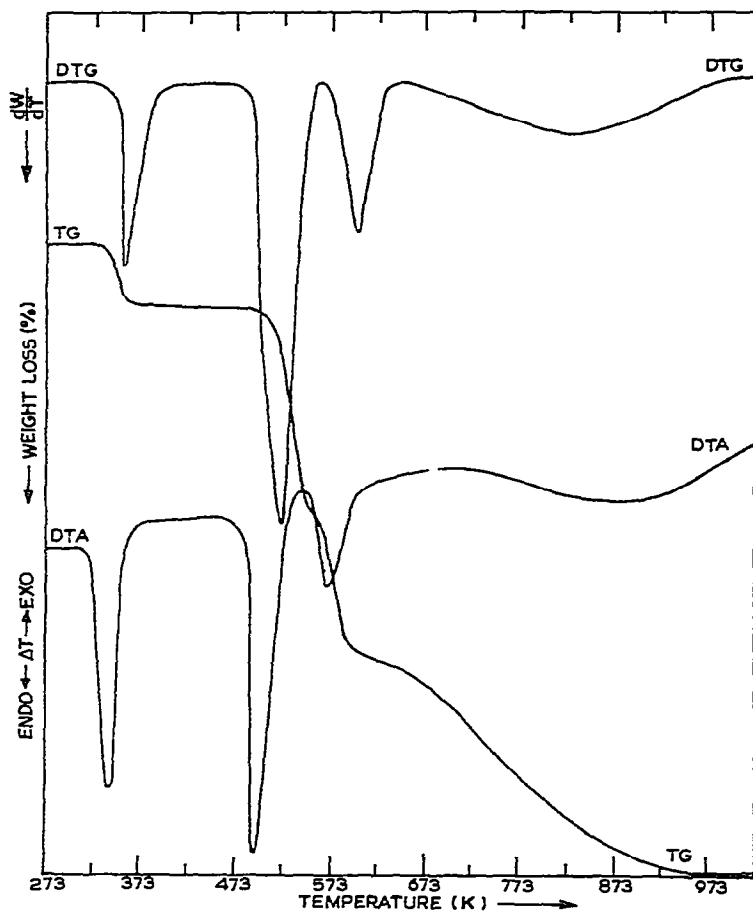
Fig. 1. DTA, TG and DTG curves for gallic acid in air.

TABLE 1

Analysis of the thermogravimetric curve for gallic acid

Decomposition step	Calc. wt.loss (%)	Observed wt. loss in TG (%)	Temp. range (K)
Dehydration of gallic acid	9.6	9.6	333—403
Partial decomposition of anhydrous gallic acid evolving carbon dioxide and some water	32.9	32.4	493—563
Evolution of remaining water forming carbon residue	9.6	9.3	568—633
Final oxidation of the carbon residue	47.9	48.6	653—993

tion exists between DTA and DTG curves, indicating that all the thermal effects are accompanied by weight loss. The data for calculated and observed weight losses and the corresponding temperature ranges are given in Table 1. The different stages of the thermal decomposition of gallic acid will now be discussed.

Dehydration

The thermogram shows 9.6% weight loss, corresponding to the loss of 1 mole of water in the first step. The calculated value for 1 mole of water per mole of gallic acid is 9.6%. Infrared spectra amd chemical analysis of the samples obtained isothermally at these temperatures show that all the other groups remain unaffected.

Decomposition of anhydrous gallic acid

Thermal decomposition of the anhydrous salt as such is a multistep process. The first endothermic reaction occurs between 493 and 563 K with 32.4% weight loss, corresponding to 1 mole of carbon dioxide and 2 moles of water, followed by another endothermic peak between 568 and 633 K, corresponding to the release of an additional 1 mole of water. These changes clearly appear on the DTA curve as a large endothermic peak (503 K) followed by a small endothermic peak (555 K). The residue remaining at this stage seems to be pure carbon. The sample obtained from isothermal heating at 653 K was black, which is indicative of carbon.
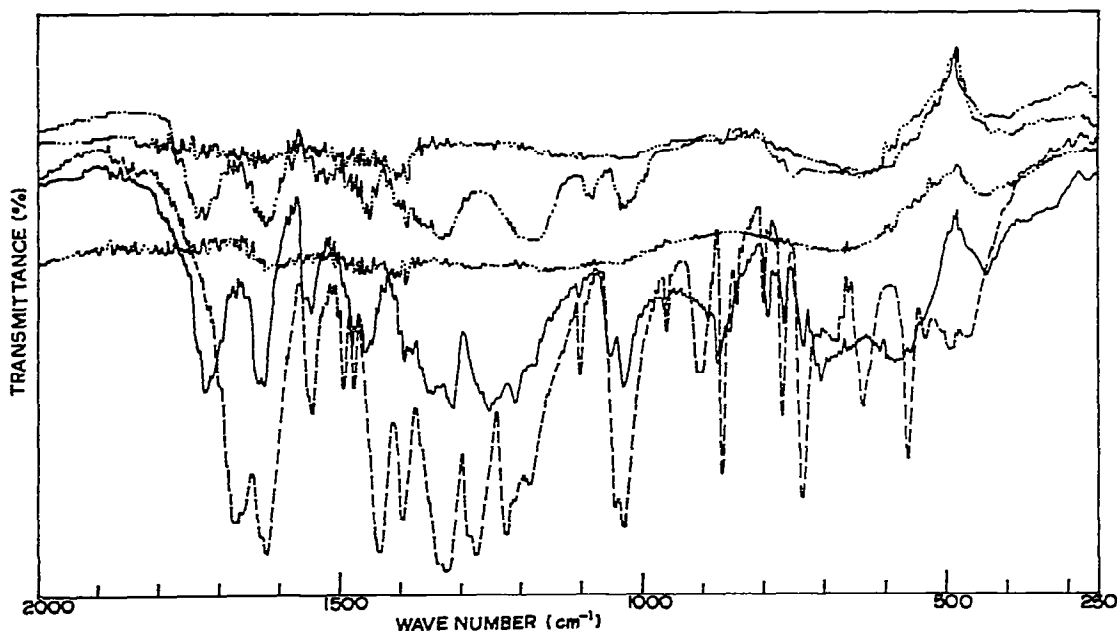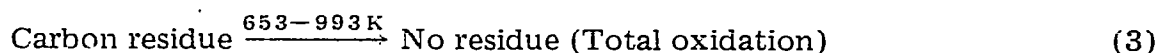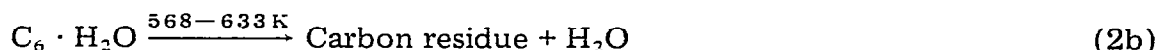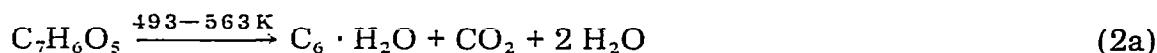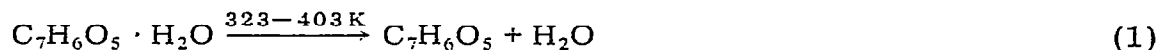

Fig. 2. IR spectra of gallic acid (————), gallic acid after dehydration (- - - - - -), gallic acid heated at 523 K (— · · —), residue obtained at 623 K (— · · —), and residue obtained at 923 K (— · · · · —).

Oxidation of carbon residue

Further weight loss between 653 and 993 K (DTG) corresponds to conversion of all the carbon residue to gases, as indicated by a complete weight loss on the thermogram. The peak corresponding to this change is also indicated on the DTA curve (870 K).

Figure 2 gives the IR spectra of various materials. The full-line spectrum in Fig. 2 shows the principal band $\nu(C=O)$ of gallic acid monohydrate at 1720 cm^{-1}, other bands may be assigned to different normal modes of vibrations of the other functional groups [4—6] present in the gallic acid molecule. The IR spectrum of a sample obtained at 353 K, i.e. after dehydration, shows all the bands present in the gallic acid molecule with only a slight shift in the peak positions. Infrared spectra of the samples obtained at 623 K and 923 K show no specific absorptions, indicating that the product is pure carbon. Chemical analysis of the products at these stages also supports the IR data.

All the above observations and results allow us to propose a three-stage scheme for the thermal decomposition of gallic acid.

$$C_7H_6O_5 \cdot H_2O \xrightarrow{323-403\,K} C_7H_6O_5 + H_2O \tag{1}$$

$$C_7H_6O_5 \xrightarrow{493-563\,K} C_6 \cdot H_2O + CO_2 + 2\,H_2O \tag{2a}$$

$$C_6 \cdot H_2O \xrightarrow{568-633\,K} \text{Carbon residue} + H_2O \tag{2b}$$

$$\text{Carbon residue} \xrightarrow{653-993\,K} \text{No residue (Total oxidation)} \tag{3}$$

From the above discussion it is clear that the weight loss steps in TG and the explanations based on them are limited in scope and the intermediates often may not represent stable composition. The composition of residues isolated in isothermal experiments need not and often do not tally with the apparent composition assigned by weight loss measurements during thermogravimetric analysis [7,8].

REFERENCES

1 L. Kieft and G.C. Chandlee, Ind. Eng. Chem., Anal. Ed., 8 392 (1936).
2 C. Mayr, Monatsh. Chem., 77 (1947) 65.
3 J.O. Gomez, and J.G. Romero, Tecnica Metal. (Barcelona), 4 (1948) 461; Chem. Abstr., 43 (1949) 4972.
4 K. Nakanishi, Infrared Absorption Spectroscopy — Practical, Holden-Day, San Francisco, 1962.
5 C.N.R. Rao, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, London, 1963.

6 R.M. Silverstein, C.G. Bassler and T.C. Morrill, Spectrometric Identification of Organic
   Compounds, John Wiley, New York, 1974.
7 V.B. Reddy and P.N. Mehrotra, Thermochim. Acta, 31 (1979) 31.
8 V.B. Reddy and P.N. Mehrotra, Thermochim. Acta, 31 (1979) 249.