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EMISSION THERMOPHOTOMETRY. IV. CELLULOSE AND SOME CELLULOSE DERIVATIVES *

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ABSTRACT

The technique of emission thermophotometry (ETP) was used to characterize cellulose and some cellulose derivatives. In this technique, the light emitted by the sample is recorded as a function of temperature, as the sample is heated at 20°C min^{-1}. The effect of heating rate on the ETP curves of ethyl cellulose was determined. It was found that the peak maximum temperature increased from 220°C at 5°C min^{-1} to 250°C at 20°C min^{-1}. Each ETP curve was unique for the cellulose samples and could be used for their qualitative characterization.

INTRODUCTION

The light emission of organic compounds, as well as polymers and natural products, has been of interest in this laboratory for a number of years. Greatly improved light emission curves can be obtained by use of a new apparatus recently described [1]. To distinguish these measurements from previous data, the term "emission thermophotometry" (ETP), is used to describe the non-isothermal, thermal analysis technique [2]. In this technique, the light emission of the sample is recorded as a function of temperature, as the sample is heated at a constant rate of temperature increase. Thus far, each sample investigated has been characterized by a unique ETP curve in the temperature range from 200 to 400°C, in a flowing oxygen atmosphere. Many of the curves contain multiple peaks caused by simultaneous or competitive light emission reactions. In most cases, the origin of the light emission process is not known. The decomposition pathway, however, may be ascertained by the use of other thermal analysis techniques such as TG, DTA, DSC, EGA, and so on.

In continuing with this series, the ETP curves of cellulose and some cellulose derivatives are presented.

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* For Part III, see W.W. Wendlandt, Thermochim. Acta, 101 (1986) 89.

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EXPERIMENTAL

Apparatus

The ETP apparatus employed has previously been described [2]. The microcomputer data logging, display and printing system provided improved recording and print-out of the light emission curves. Variable scaling was permitted on both the light emission and temperature axes, as well as other manipulative features.

Procedure

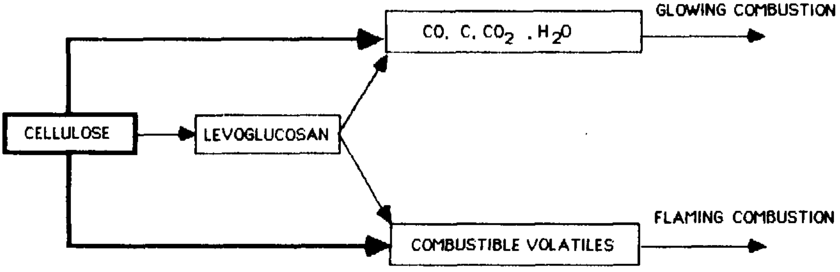
The cellulose samples, with masses ranging from 2 to 10 mg, were heated from ambient room temperature to about 400°C at a heating rate of 20°C min^{-1} (or lower) in a flowing oxygen furnace atmosphere (30 ml min^{-1}). Except for the cellulose sample, the samples consisted of a microgranular powder, which were placed in 7 mm diameter aluminum sample holders. No background corrections were needed for the ETP curves.

Samples

The cellulose derivatives investigated were obtained from Scientific Polymer Products, Inc., Webster, NY. They were used without further modification or purification.

RESULTS AND DISCUSSION

The thermal decomposition of cellulose in oxidizing and non-oxidizing atmospheres has been studied by numerous investigators [3–6]. In oxidizing atmospheres, the general scheme appears to be [3,4]:



Oxygen has an effect on the final products but not on the overall pattern of behavior. Varying the atmosphere may cause a different pathway to be favored, but the general scheme remains the same. Other factors which can affect the reaction path are temperature, period of heating (including the heating rate), and the physical and chemical properties of the cellulose. Wodley [5] found that the degradation processes of cellulose in inert and oxidizing atmospheres were identical. In the decomposition of cellulose, the breakdown proceeds so rapidly that the accompanying slow oxidation of the cellulose is completely overshadowed. For temperatures below 200°C, the slow oxidative reaction predominates but at higher temperatures, the principle reaction is depolymerization of the cellulose to form levoglycosan (1,6-anhydro-β-D-glucopyranose).

Dollimore and Hoath [3], using DTA, found that the pyrolysis of cellulose in air produced two and sometimes three exothermic peaks. The first peak (~ 345°C) was associated with the combustion of volatile matter, released in the degradation process. The second peak (~ 460°C) was caused by the glowing combustion of the carbonaceous residue, while the final peak (530°C) was probably due to the combustion of product gases. Increasing the heating rate resulted in: (a) an increase in peak widths; (b) an increase in peak temperature; (c) more detail of the curve peaks; and (d) a poor return to baseline between major peaks. A heating rate of 10°C min^{-1} appeared to be the most suitable and was adopted for their studies.

Wendlandt [7], who previously characterized the light emission of a series of cellulose derivatives, found that most of the compounds had curve peaks in the 150–350°C temperature range. The only exception appeared to be cellulose triacetate with a curve peak between 350 and 400°C.

The ETP curves of cellulose and some cellulose derivatives are shown in Fig. 1.

The ETP curve of pure cellulose (A and B) (Whatman No. 1 filter paper) consisted of a single peak with a peak maximum of about 280°C, some 65° below the DTA peak maximum temperature [3]. Thus, the light emission process takes place at a much lower temperature than that for combustion. Also, the light emission intensity was very low, far less than that given off during the combustion process. An expanded drawing of the curve peak is shown in (A) which reveals the details of the peak. The origin of the light emission peak in cellulose is not known but it may be similar to that discussed previously by Wendlandt [8] for polyethylene and polypropylene. This mechanism involved the formation of peroxy radicals which terminate into electronically excited ketone products. A transition of the type $n \rightarrow \pi^*$ can give rise to phosphorescence.

The light emission of ethyl cellulose was much greater than that of pure cellulose, as shown by the ETP curves in (C), (D) and (E). To determine the effect of heating rate on the curve peak maxima temperatures, the ETP curves of ethyl cellulose were determined at 5, 10 and 20°C min^{-1}. As expected, the peak maxima increased from 220°C at 5°C min^{-1}, to 250°C at 20°C min^{-1}. Also, on increasing the heating rate, the curve peak became broader.

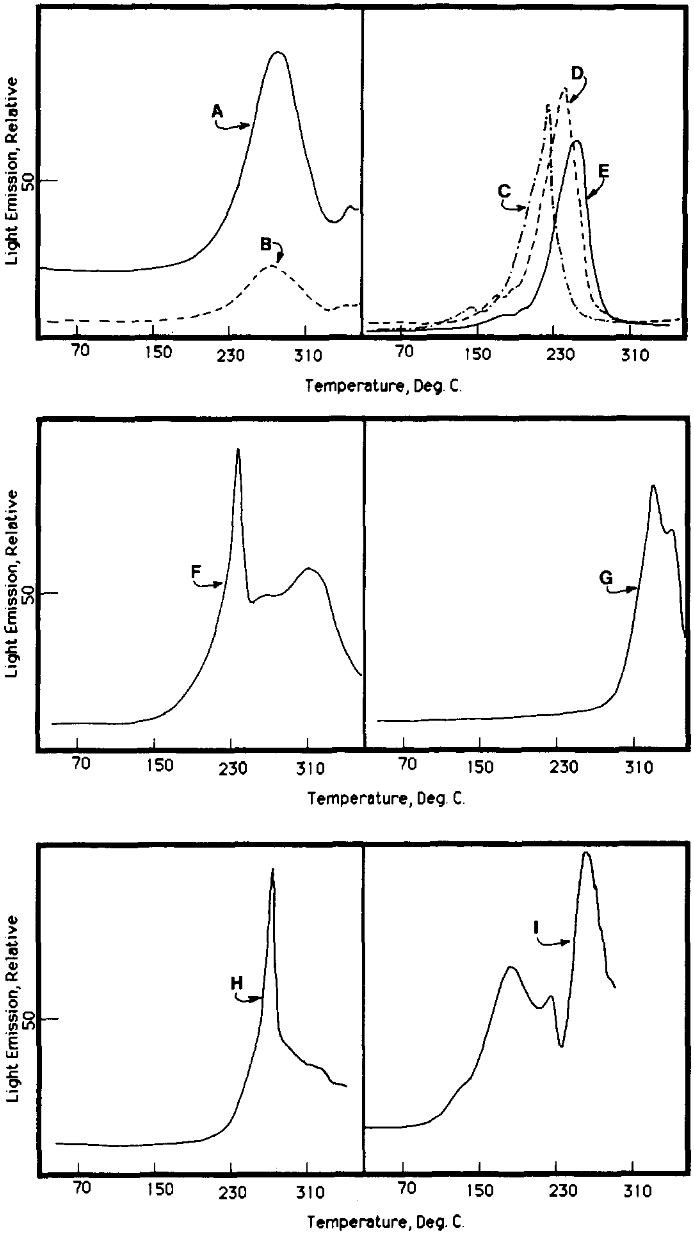


Fig. 1. ETP curves of (A) cellulose, scaling factor of 25; (B) cellulose, scaling factor of 100; ethyl cellulose at (C) 5°C min^{-1}, (d) 10°C min^{-1}, and (E) 20°C min^{-1}; (F) cellulose acetate butyrate, scaling factor of 33.3; (G) cellulose propionate, scaling factor of 20; (H) cellulose acetate, scaling factor of 100; and (I) cellulose triacetate, scaling factor of 100.

Of the remaining cellulose derivatives (F to I) multiple peaks were found in three of them. A very narrow peak at 280°C was observed for cellulose acetate (H) while in cellulose triacetate (I), multiple peaks were observed, with the main peak maximum at 260°C. The latter is a good example of a compound that exhibits multiple light emission processes.

The main peak in the ETP curve of cellulose acetate butyrate (F) is at 250°C, which is followed by a broad peak maximum at 315°C. The most stable of the cellulose derivatives appears to be cellulose propionate (G), which has a light emission peak maximum at 330°C.

As in previous ETP studies, the resulting light emission curves appear to be unique for each compound investigated. Thus, the curves may be useful for the qualitative characterization of these compounds. The ETP technique is simple in principle and practice and the time involved is of the order of 20–25 min.

ACKNOWLEDGMENT

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