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SOME FEATURES OF DTA IN PLATINUM CRUCIBLES

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Some features of DTA in platinum crucibles in air related to the catalytic activity of platinum in many oxidation reactions have been considered. This property of platinum should be taken into account in the interpretation of the DTA curves.

The high thermal stability and corrosion resistance of platinum ensure its wide use as a material for manufacturing precise chemical instruments [1]. In particular, it is considered to be a very convenient material for the manufacture of sample holders in thermal analysis, especially for high-temperature work. Berg [2], Wendlandt [3] and other workers have mentioned platinum sample holders. However, researchers in the field of thermal analysis point out as the major advantage of platinum its chemical inertness, but usually forget its other very important property: its catalytic activity in many organic and inorganic reactions [4]. The disregard of this property can lead to serious mistakes in thermal analysis. The present paper considers some effects due to the use of platinum crucibles in DTA in an atmosphere of air.

Experimental

DTA was carried out with a modified DTA instrument based on a derivatograph MOM, Hungary.

The sample was placed in an open platinum crucible of a standard set supplied by the MOM company with the derivatograph. A glass crucible of the same shape was prepared from pyrex glass. All experiments were carried out in a static atmosphere of air; the rate of the temperature rise was 10°/min.

Reagent grade calcium oxalate, $CaC_2O_4 \cdot H_2O$, was used without further treatment; polymer samples (polyacrylonitrile and cellulose) were provided by the laboratories of the Institute of Macromolecular Compounds of the Academy of Sciences of the U.S.S.R.

Discussion of results

Figure 1 shows the results of the DTA of calcium oxalate ($CaC_2O_4 \cdot H_2O$). Curve 1 represents DTA carried out by using a platinum crucible precalcined in a Bunsen burner. Subsequent experiments were carried out under the same condi-

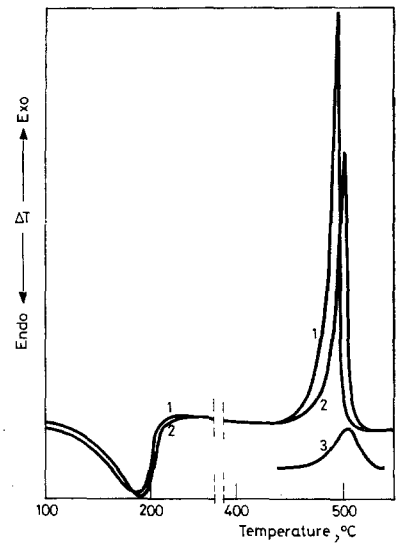

Fig. 1. DTA curves for $CaC_2O_4 \cdot H_2O$: 1. platinum crucible immediately after calcination, 2. platinum crucible after seven successive analyses, 3. glass crucible

tions, but without calcination. Comparison of the DTA curves shows that both the area and the temperature of the endothermic peak with maximum at 190°, characterizing the dehydration of the monohydrate of calcium oxalate, remain virtually unchanged.

As concerns the exothermic effect of decomposition of the dehydrated oxalate according to the reaction:

$$CaC_2O_4 \rightarrow CaCO_3 + CO$$

the quantitative parameters of this reaction are directly dependent on the catalytic activity of the platinum crucible.

The calcination of a platinum crucible on a Bunsen burner leads to the activation of its surface. When the analysis was repeated many times, the surface of the platinum was gradually poisoned with CO_2 and the area of the exothermic peak decreased as the duration of the experiment increased. At the same time, the maximum of the exothermic peak shifted towards higher temperatures and after eight successive experiments the difference between the peak maxima for the first and the eighth experiment exceeded 10° (Fig. 2). In this connection it should be borne in mind that when the platinum crucible was replaced with a glass crucible the same series of eight experiments of DTA of calcium oxalate yielded coinciding exothermic peaks with a maximum at 500° (Fig. 1, curve 3). The quantitative treatment of DTA data relating to the oxidation reaction can lead to serious errors if a possible change in the catalytic activity of the platinum is not taken into account.

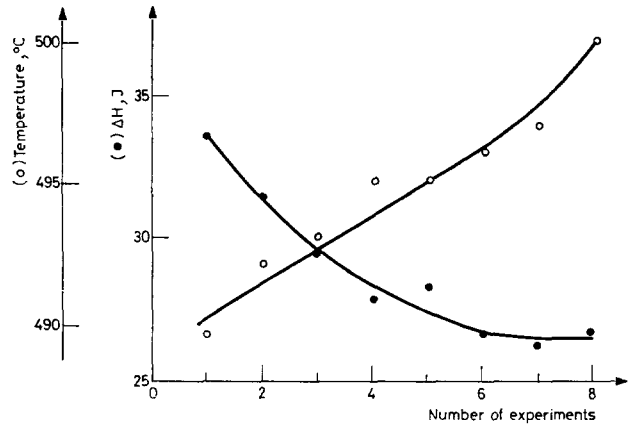

Fig. 2. Heat evolution and temperature of the maximum of the exothermic peak *vs.* number of successive analyses in a platinum crucible in the DTA of $CaC_2O_4 \cdot H_2O$

It is well known [5, 6] that in the thermal analysis of polymers the methodological conditions of the experiments in most cases determine the development of the thermochemical processes occurring in the polymers on heating. Hence, the catalytic activity of platinum can greatly distort the DTA pattern of polymers not only quantitatively, but also qualitatively. Figure 3 shows DTA data for a polyacrylonitrile (PAN) sample. Curve 1, obtained by using a platinum crucible, exhibits two exothermic peaks (t_{max_1} = 314° and t_{max_2} = 381°). At first sight this fact indicates the existence of two stages of thermal transformation of the sample. However, if a glass crucible is used as sample holder (curve 2), it is clear that only the peak at t_{max} = 314° represents the transformation proper of the polymer, whereas the second peak is due to the catalytic oxidation of secondary products of PAN degradation.

Another example of the catalytic activity of platinum in the thermal analysis of polymers is the result of the DTA of cellulose. In this case one can speak about a certain positive part played by the platinum, as it markedly activates the thermochemical processes of oxidation and thus increases the sensitivity of the DTA, so that the experiments become more informative.

Thus, a sharp increase in the height of the exothermic peak when a platinum crucible is used, as compared to its height obtained with a holder manufactured of another material, indicates that this peak corresponds to the oxidative reaction. Figure 3 shows an example of the exothermic effect caused by the oxidation of cotton fibre. For the same weight of sample (5 mg), the use of a glass crucible led to a slight exothermic effect with a maximum at 350°, whereas the height of the same peak in DTA carried out in a platinum crucible exceeded the limits of the recorder scale.

In conclusion, it should be noted that the catalytic effect of platinum in oxidation reactions in DTA in air begins to appear only above a certain temperature. In the

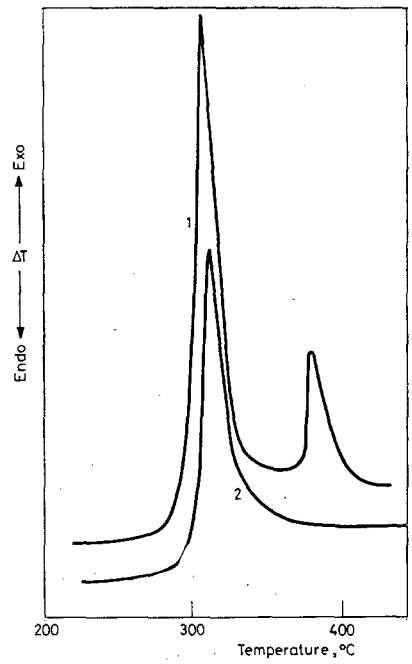

Fig. 3. DTA curves of polyacrylonitrile: 1. platinum crucible, 2. glass crucible

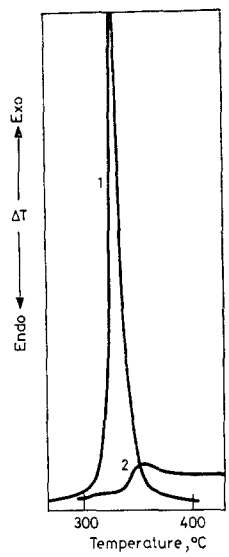

Fig. 4. DTA curves of cotton fiber: 1. platinum crucible, 2. glass crucible

examples given above, the temperature of about 310° is the threshold temperature of platinum activity.

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