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INVESTIGATION OF THERMAL DEGRADATION OF POLYSTYRENE WITH THE AID OF THERMAL ANALYSIS

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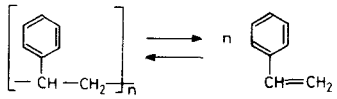
When the DTA of polystyrene is carried out in air in a platinum sample holder, an anomalously high endothermic effect is observed. This effect was found to be related to gas-phase catalytic styrene oxidation occurring on the surface of both operating and reference platinum sample holders. Methodological recommendations are given concerning the DTA procedure for organic substances, making it possible to avoid this type of anomaly.

The thermal degradation of polystyrene (PS) has been fairly well investigated. It is known that this process occurs mainly as depolymerization, as a result of which the initial monomer, styrene, is evolved:



(1)

to the accompaniment of an endothermic effect [1, 2].

In fact, if analysis is carried out in a ceramic crucible in a static atmosphere of air (derivatograph, heating rate 10 deg/min, sample weight 50 mg), the DTA curve of powdered PS exhibits a weak endothermic peak with a maximum at 394°, followed by two small exothermic peaks with maxima at 420 and 542° (Fig. 1, curve 1). However, when a ceramic crucible is replaced by a platinum crucible, the endothermic effect increases markedly (Fig. 1, curve 2). This increase cannot be related to the different thermal conductivities of platinum and ceramics, for if the analysis is carried out in ceramic and platinum crucibles in an inert atmosphere (He), the corresponding peaks are comparable (Fig. 1, curves 3 and 4, respectively).

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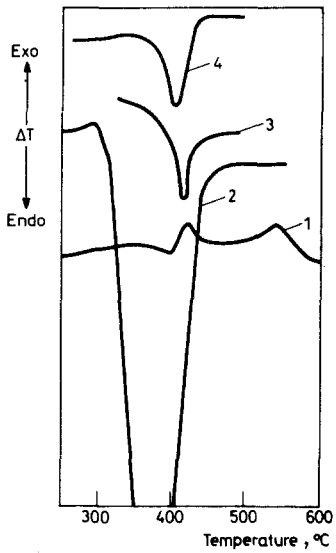
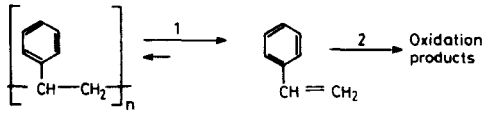


Fig. 1 DTA curves of PS in a static atmosphere of air (1, 2) and helium (3, 4): 1, 3 – in a ceramic crucible and 2, 4 – in a platinum crucible

As has already been indicated [3–6], the ability of platinum to catalyze many oxidation reactions of both organic and inorganic substances should be taken into account when thermal analysis is carried out with platinum holders. However, oxidation reactions are usually exothermic, and hence at first sight the case under consideration does not obey the relationships described previously, although the catalytic effect of platinum in the observed process is beyond doubt.

In order to elucidate the way in which platinum catalyzes the depolymerization of PS, the DTA of the gaseous product of PS degradation was carried out under the conditions os catalytic oxidation on platinum. It was found that the styrene evolved in this process is strongly oxidized on the platinum surface, and oxidation is accompanied by high exothermic effect, comparable in magnitude to the observed endothermic effect of PS degradation (Fig. 2). The scheme of reactions occurring in this system may evidently be represented by the following scheme:



(2)

The depolymerization of PS is known to be reversible. The catalytic oxidation of styrene on platinum according to reaction 2 occurs very rapidly, and as a result the

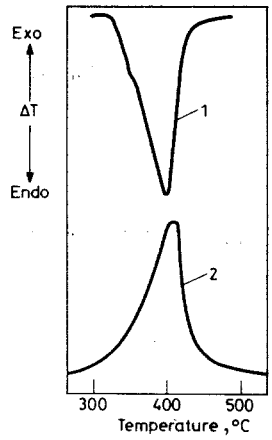


Fig. 2 DTA curves of PS in a static atmosphere of air: 1 – overall peak of thermal degradation, 2 – peak of gas phase styrene oxidation

styrene concentration in the reaction zone is maintained at a very low level and Eq. 1 is markedly displaced to the right according to the Le Chatelier principle.

However, the above considerations do not explain the drastic increase in the peak area in the PS analysis carried out in a platinum crucible. The area under the peak corresponding to the heat of degradation evidently should not depend on the reaction rate, and hence the area under the peak obtained in DTA carried out in a ceramic crucible should not (taking into account a correction for thermal conductivity) differ from that for DTA carried out in a platinum crucible.

This contradiction can be explained if it is considered that, according to the usual scheme, two identical holders are present in the thermoanalytical cell: one of them contains the sample under investigation, and the other contains the reference sample. When platinum holders exhibiting catalytic activity are used for both samples, it may be expected that the gas-phase oxidation reaction will proceed on the surface of both the operating and the reference holder. Moreover, if the surface of the operating crucible is poisoned with the polymer which is in the liquid phase at the temperature of thermal degradation, and with the products of styrene oxidation dissolved in this polymer, then only the gas-phase reaction of styrene oxidation proceeds on the surface of the reference crucible. In this case the mass exchange is more pronounced and the platinum surface is poisoned to a much lesser extent.

It is evident that the high endothermic effect observed in this case is essentially only a "reflection" of the exothermic effect of the gas-phase styrene oxidation occurring on the surface of the platinum crucible of the reference sample. In fact, when this sample was placed in an inactive ceramic crucible, and the sample under investigation was placed in a platinum crucible, the DTA curve exhibited a strong

exothermic peak of styrene oxidation, completely absorbing the endothermic effect of its formation from PS (Fig. 3).

If the thermoanalytical cell is flushed with air (25 l/h), thereby increasing the mass exchange on both crucibles, at high temperatures the surface of the operating crucible is reactivated and in the DTA curve the descending branch of the observed endothermic peak passes into a very narrow exothermic peak (Fig. 3, curve 2).

Hence, it was again demonstrated that in the interpretation of thermal analysis data all the methodological features of the procedure should be taken into account. If platinum crucibles widely used in thermal analysis are employed, the concept "reference sample" may lose its meaning, when a gas-phase oxidation reaction catalyzed by platinum can occur in the system. In the analysis of organic substances, this situation is very common. Hence, in order that the reference sample may serve its purpose, it should be placed in a holder made of inactive material (ceramics, glass, etc.).

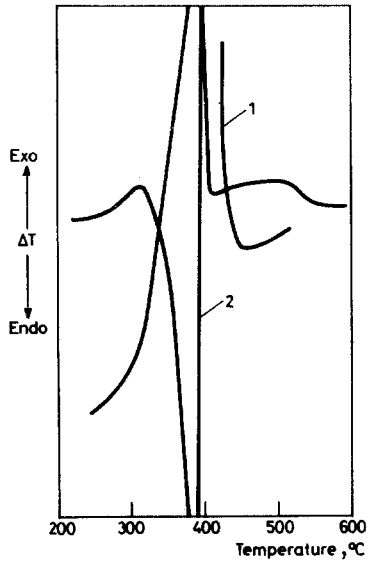


Fig. 3 DTA curves of PS: 1 – in a static atmosphere of air (platinum operating crucible and ceramic reference crucible, 2 – in an air flow of 25 l/h (both crucibles are made of platinum)

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