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DETERMINATION OF MALEIC ACID AND FUMARIC ACID IN THE PRESENCE OF EACH OTHER BY THERMAL ANALYSIS

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The thermal properties of fumaric acid and maleic acid were investigated. It was found that differences in their thermal decompositions provide a possibility for their determination. The thermoanalytical determination of their mixtures was carried out derivatographically.

There is relatively little possibility of the quantitative determination of maleic acid and fumaric acid in the presence of each other. Their determination is possible in general only after their previous separation. A possibility without separation is offered, however, by the polarographic method [1].

In the course of an investigation of their syntheses and isomerization it seemed practical to carry out the determination from thermal characteristics.

We have carried out several derivatographic examinations [2] in an air atmosphere to study the behaviour of fumaric and maleic acids submitted to heat effects. (The weight of sample was about 100 mg, and the heating rate was 3°/min.)

The derivatogram of maleic acid (Reanal) shows that simultaneously with melting the sample begins to disappear (Fig. 1, dashed curve).

The process can be seen from the DTA curve to be endothermic and thus an oxidative decomposition is improbable; we assume that soon after melting the sample evaporates rapidly from the sample holder. The reproducible peak in the initial stage of the DTG curve is probably due to the fact that after a small amount of the sample has melted, i.e. after the partial formation of the melt phase, the rate of departure of maleic acid is slightly reduced; however, it rises again with increasing temperature and no appreciable residue remains above 200°.

The endothermic transformation of fumaric acid (Reanal) occurring at 205° on the DTA curve in Fig. 1 (continuous curve) is not accompanied by any change of weight. Our supplementary microscopic investigations revealed that this process is the transformation of prismatic fumaric acid to monoclinic fumaric acid. Subsequently, above 210°, fumaric acid begins to sublime.

It should be noted that Wendlandt did not mention this effect of fumaric acid in his DTA investigation [3], although an endothermic peak appears on the curve in this temperature range.

The different thermal behaviour of maleic and fumaric acids provides a possibility of determining them in the presence of each other.

From the above it may be seen that the total maleic acid departs before the beginning of the sublimation of fumaric acid.

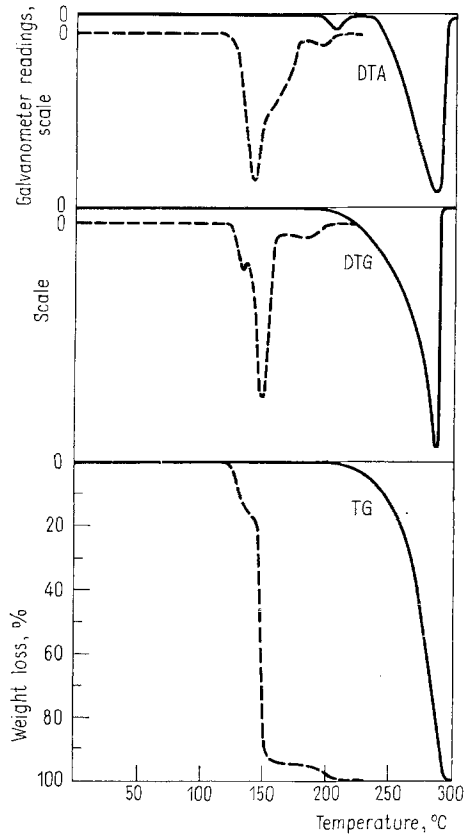

Fig. 1. Derivatograms (TG, DTG and DTA curves) of maleic acid and fumaric acid

In the course of our work we tested mixtures of maleic and fumaric acids of varying composition and observed that in each case the decomposition curves showed the differences in thermal properties of the two isomers which permitted their determination in the presence of each other.

Fig. 2 presents the derivatogram of one member of our test series, a mixture of 70% fumaric and 30% maleic acid, showing the possibility of determination from the well-separated decomposition steps.

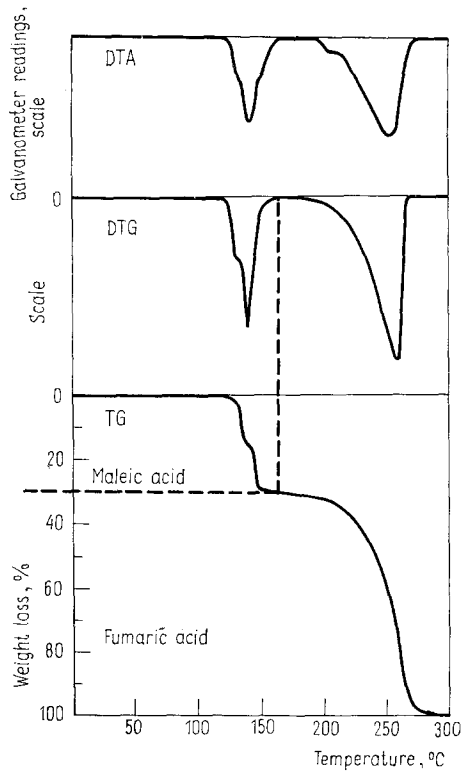

Fig. 2. Derivatogram (TG, DTG and DTA curves) of a mixture of fumaric acid and maleic acid (70 and 30%)

References

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