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Note

The effect of grinding on DTA curves of silver nitrate

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A few examples of the effect of grinding on DTA curves have been reported[1-4]. The two types of the effects are elucidated till now; one is the effect on the physical transition and fusion, and the other is the effect on the reaction kinetics. In the course of calibrating a new apparatus of quantitative differential thermal analysis reported elsewhere[5], the similar effect of grinding, but somewhat different from those reported till now, has been revealed on the transition and the fusion of silver nitrate, and it is reported in this short communication.

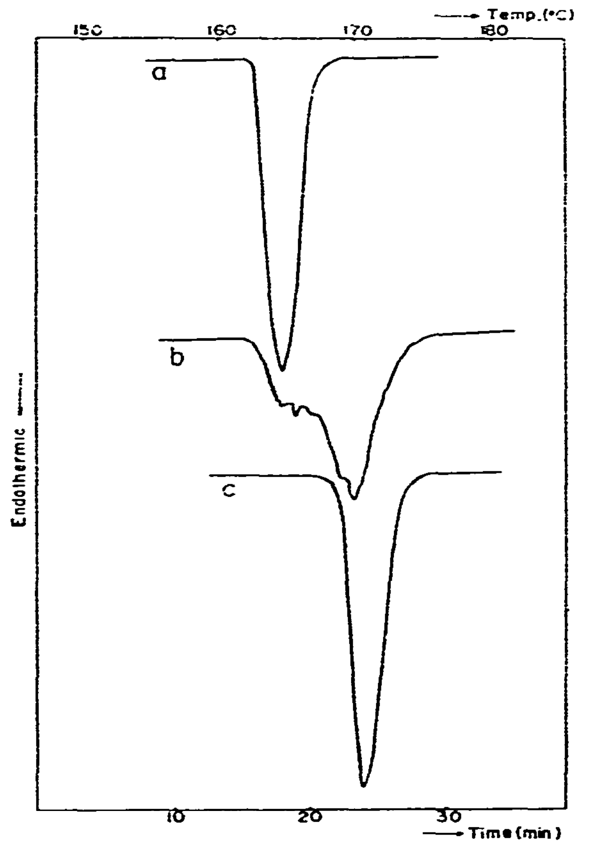

Fig. 1. The DTA curves obtained at the crystalline transition of silver nitrate. a, the original sample; b, the slightly ground sample; c, the finely ground sample.

The DTA curve of the transition at about 161 °C obtained with the original sample is shown in Fig. 1(a), which is a normal DTA curve, while the curve observed with slightly ground sample is an extraordinary one, as is shown in Fig. 1(b). If the sample is ground finely, the peak of the curve is an ordinary sharp one, as is shown in Fig. 1(c). However, the transition temperature of the finely ground sample is 166.5 °C, and higher than that of the original sample by 5.5 °C. The DTA curve of the finely ground sample does not depend on the heating rate in its nature, and the transition temperature is also independent on the heating rate in the range from 30 °C/h to 120 °C/h. If the sample is cooled immediately after the peak of the transition and reheated, the curve obtained does not change essentially. But, if the sample is once melted, the curve obtained by reheating it is the same as that of the original sample.

On the other hand, the grinding have an effect also on the melting behavior. As is shown in Fig. 2, the peak of finely ground sample is sharp, especially in its beginning, while the fusion begins at somewhat lower temperature for the other samples. It may be necessary to note that grinding increases both temperatures of the transition and fusion of silver nitrate, while it is usually observed that grinding produces decrease in the temperature of transformation.

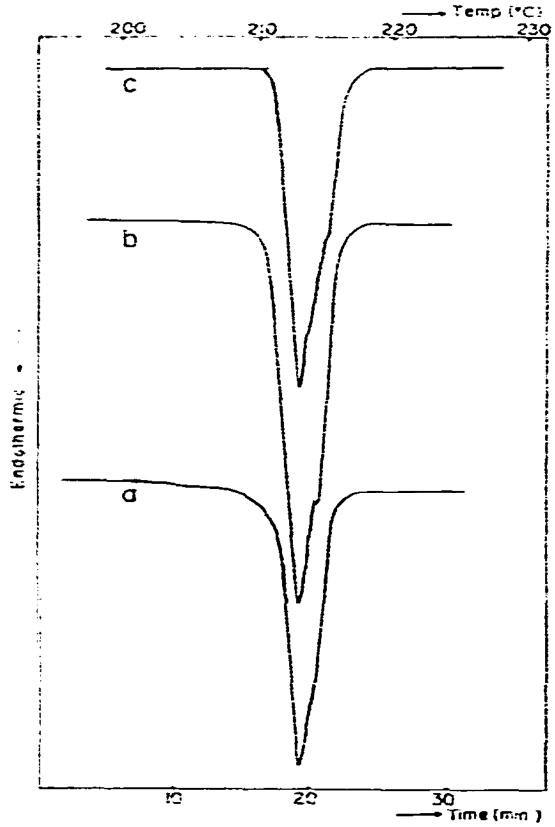

Fig. 2. The DTA curves obtained at the melting of silver nitrate. a, b and c are the same as in Fig. 1.

The curves of these samples does not change essentially, when they are left in the desiccator above silica gel for a few months. The latent heats of both transformations are observed to be indifferent among the samples within the experimental error. The X-ray diffraction patterns of these samples are obtained by Geigerflex (Rigaku Denki Co. Ltd.), and the diffraction lines are in accordance with ASTM card; a new phase is not observed in both of ground samples. However, 2θ of some diffraction lines seem to shift; some to the lower value and the other to the higher value.

It would be infered from the above-mentioned facts that the effect of grinding on the transition is a kinetical one, namely the formation of the barrier to the transition. The discrepancy of the transition temperature and the melting temperature reported in the previous paper and in the papers of the other authors seems to be caused by this effect.

The differential thermal analysis was made with the apparatus reported elsewhere[5] in an ambient atmosphere. The original sample is G. R. grade purchased from Showa Chemical Co. Ltd., and it was ground in a mortar by hand for about 15 min and 1 h in an ambient atmosphere for the slightly and finely ground samples, respectively.

The same effects of grinding are also observed with a Perkin–Elmer DSC under the flow of dry nitrogen, and with a DSC manufactured by Rigaku Denki Co. Ltd. in an ambient atmosphere.

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