Polymorphic Transitions in Anhydrous Sodium Sulphate

THE heat capacity of anhydrous sodium sulphate has been measured recently in a water calorimeter by Kreidl and Simon¹, who observed only one hightemperature transition, at about 238°C. However. there are two known polymorphic transitions between room temperature and 300° C. : (1) the transformation of the stable low-temperature form V to the intermediate form III and (2) transformation of III to the stable high-temperature form I. The heat of transition observed by Kreidl and Simon was nearly equal to the sum of the heats of the two known transitions. They concluded that in the presence of water, the transition $V \longrightarrow I$ occurs directly and reversibly, and supported this conclusion with X-rav diffraction data. More recently, Bird² has reported an irreversible transformation, $V \longrightarrow I$, upon heating sodium sulphate in the absence of water. This occurred at a considerably lower temperature of about 176° C., and is based on comparison of high-temperature X-ray diffraction patterns.

We have now subjected anhydrous sodium sulphate (reagent grade) to differential thermal analysis in the absence of water, using a high-sensitivity apparatus³. The rate of heating was maintained constant at 12 deg. min.⁻¹ over the entire range $25-350^{\circ}$ C.; however, it was not possible to control the rate of cooling so closely. The curves are shown in Fig. 1. It should be noted that the reaction peak temperatures are by no means absolute, but are constant only for a given set of experimental conditions.

Only one transition peak was observed in the differential thermal analysis curves, beginning around 235° C. on heating. The transition is completely reversible, even though the sample was free of water. The areas under the peaks, which are proportional to the heats of the reaction involved, are of the same



Fig. 1. Differential thermal analysis curves of anhydrous sodium sulphate between 25° and 350° C. (a) Heating curve, (b) heating curve obtained after cooling the sample (a) to 25° C.; (c) heating (solid line) and cooling (dotted line) curves

order of magnitude for both the endothermic (heating) and exothermic (cooling) peaks.

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C. N. R. RAO L. V. GREGOR

Department of Chemistry. University of California, Berkelev 4. Feb. 23.

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BIOCHEMISTRY and PHYSIOLOGY

Proton Transfer and Supercontraction in Actomyosin

It has been previously reported that the synaeresis of actomyosin gels with adenosine triphosphate is accompanied by changes in the X-ray diffraction pattern indicating that some part of the actinmyosin complex undergoes supercontraction¹. The recent observation by Goodall² that one or more protons at each active site are involved in the production of tension in the myofibril is in line with my experiments, which suggest that the supercontraction of myosin (or actomyosin), long postulated as the fundamental basis of muscle contraction³, might also be due primarily to some specific transfer of protons.

Earlier investigation showed that actomyosin apparently supercontracted on acidification, but the drastic nature of the treatment (2 per cent acetic acid) did not preclude the possibility of artefacts from partial hydrolysis. More recently, however, I have succeeded in preparing films of actomyosin from very weakly acid dispersions of the gel, and from neutral films weakly acidified and washed at neutrality, that show the characteristic reflexion at 4.65 A. on the meridian of the X-ray diffraction diagram. In every case, the hydrogen ion, rather than any anion combination of chloride, phosphate and acetate, appears to be responsible for the change.

The transformation into the supercontracted state, as judged by this test, becomes detectable below pH 6.0. Thixotropic gels of actomyosin allowed to stand for 48 hr. at pH 5.0, for example, form insoluble precipitates indistinguishable from those formed on addition of adenosine triphosphate at neutrality. When actomyosin from fish dorsal muscle is dried from a slightly acidified dispersion of the gel, the X-ray diffraction diagram is always characterized by a marked cross- β pattern, and at pH values in the region of 5.0 the meridional reflexion at 4.65 A. predominates over the 5.1 A. α -reflexion. Again, the X-ray diffraction diagrams of similarly prepared actomyosin gels dried at neutrality show a progressive increase in the cross-ß pattern with increasing acidification and time of treatment. Immersion of the films at pH 5.0 for 48 hr., for example, followed by washing at neutrality, drying and mounting, results in the appearance of a clear supercontracted component after orientation by stretching (Fig. 1).

The ease with which these small changes of pH bring about the X-ray signs of supercontraction in actomyosin suggests that the system is extremely sensitive to protons. It might be argued that although adenosine triphosphate induces supercontraction at