860. *The Decomposition of Barium Styphnate Trihydrate.*

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The kinetics of the decomposition of the anhydride of barium styphnate trihydrate have been investigated. The marked differences found between the behaviour of this anhydride and that derived from the monohydrate show that the kinetics and, to a less extent, the activation energy are dependent on the topography of the reactant matrix.

As far as the authors are aware, the thermal stability of barium styphnate trihydrate, particularly in relation to the monohydrate, has not as yet been investigated. We report here a kinetic study of the isothermal decomposition of the trihydrate and compare the results with those obtained in our investigation of the dehydration and decomposition of the monohydrate,[1] where references to experimental techniques can be found.

The gamboge-coloured trihydrate is much easier to dehydrate than the monohydrate; the latter dehydrates slowly above 110° *in vacuo* with an activation energy of 26 kcal./mole, whereas the trihydrate loses all its water of crystallisation *in vacuo* in 20 min. at room temperature. On subsequent exposure to air, the reddish-brown anhydride so formed takes up one molecule of water to form a stable monohydrate which is indistinguishable by *X*-ray analysis from that obtained from solution. Similarly, the dehydration and decomposition characteristics are identical with those previously reported for the " normal " monohydrate. It may be noted that trihydrate stored under normal conditions in laboratory air slowly changes over a two-year period to a bright lemon-yellow indicating superficial conversion into the monohydrate on storage.

Fig. 1. *Typical plots of pressure against time. The lowest curve refers to an " interrupted " run.*

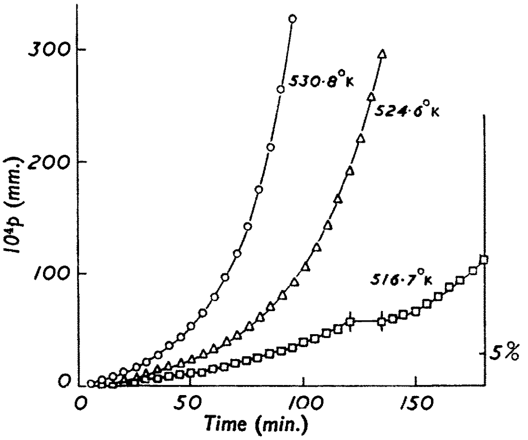
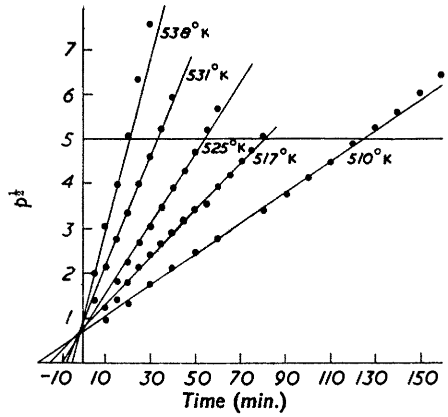


Fig. 2. *Plots of* $p^{\frac{1}{2}}$ *against* t *for a series of runs at different temperatures.*



The main interest here was whether the anhydride formed by rapid low-temperature dehydration of the trihydrate would decompose thermally in the same way as the anhydride formed by the higher-temperature dehydration of the monohydrate, it having previously been shown[1] that dehydration of the monohydrate is complete at its decomposition temperature. Decomposition of the " trihydrate anhydride " proceeds smoothly between 236° and 265° and above 265° explosion normally occurred, whereas the temperature range for the smooth decomposition of the " monohydrate anhydride " is higher, *viz.*,

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[1] Young and Tompkins, *Trans. Faraday Soc.*, 1956, **52**, 1245.

269—308°, and explosions occur for whole crystals above 300° after about 45% decomposition. Similarly, marked differences are found in the kinetics of decomposition of the two forms.

Typical pressure against time plots for the decomposition of the "trihydrate anhydride," including an interrupted run, are given in Fig. 1. We have plotted these in Fig. 2 according to the equation

$$p^{\frac{1}{2}} = k(t + t_0) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

found valid in the previous investigation. Straight lines with negative time intercepts are obtained up to 5% decomposition only, with large positive deviations above, the intercept t_0 being temperature-dependent; however, for the "monohydrate anhydride," the equation was valid from 10 to 45% decomposition and t_0 was independent of temperature. The activation energy, derived from the temperature coefficient of k and also from that of $(1/t_0)$, is 33·5 ± 0·8 kcal./mole (see Fig. 3) compared with a corresponding value of 36·5 ± 0·6 kcal./mole for the monohydrate anhydride.

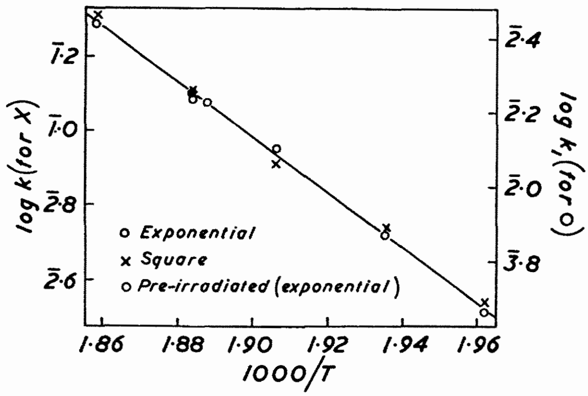

FIG. 3. *Arrhenius plots*: log k *from eqn.* (1) (*left-hand ordinate*) *and* log k_1 *from eqn.* (2) (*right-hand ordinate*) *against* 1/T (° K) *to give* E = 33·5 *kcal./mole.*

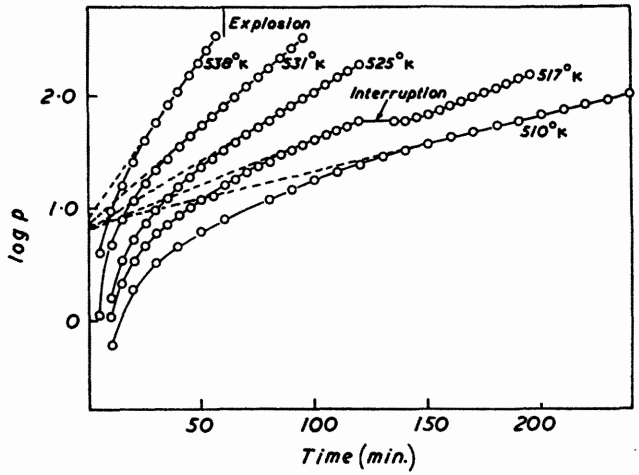

FIG. 4. *Plots of* log p *against* t—*the run at* 517° K *was interrupted.*

Above 5% decomposition, the plot of the logarithm of the pressure of gas evolved against time is a straight line but below 5% there are negative deviations from this line (Fig. 4), and the intercept at zero time is independent of temperature. The expression

$$p = C \exp{(k_1 t)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where C is a constant independent of temperature and k_1 is a rate constant, holds up to the inflexion point at about 45% decomposition. The activation energy derived from the temperature coefficient of k_1 is again 33·5 kcal./mole.

The characteristics of the thermal decomposition were unaffected by changes in the temperature of dehydration of the trihydrate or by annealing the anhydride at 120° *in vacuo*. (Annealing in the laboratory atmosphere converted the sample into the monohydrate.) Interruption of a run likewise had no effect on the rate. Although prolonged photolysis with light of λ 2537 Å caused some decomposition, pre-irradiation did not alter the rate of subsequent thermal decomposition.

These results make it evident that the anhydrous matrices obtained by the dehydration of the monohydrate and the trihydrate are physically different, that formed from the trihydrate being less stable as exemplified by the lower activation energy and lower temperature range for measurable rates of decomposition. The topochemical features which determine the rate law are apparently unchanged at 120° provided water vapour is absent; in presence of water vapour conversion into the monohydrate is easy even when the " trihydrate anhydride " had previously been heated to just below its decomposition temperature. Water clearly catalyses the conversion into the monohydrate lattice which is not produced directly from the trihydrate lattice, at least under the conditions used by us. Evidently the activation energy for rearrangement to give the monohydrate is greater than the activation energy for dehydration. Furthermore it is clear from the rapid loss of water from the crystal bulk and the relatively rapid take-up of water with formation of the monohydrate that the " trihydrate anhydride " is quite " porous." For the initial 5% decomposition there seems little reason to change the mechanism given for the decomposition of the anhydride of the monohydrate and of that of lead styphnate monohydrate.[2] The dehydrated small crystals of the trihydrate consist of blocks, the faces of which were the sub-grain boundaries of the original crystals; remnants of crystalline structure in a strained metastable condition persist within each block. Nucleation of the sub-grains occurs at the lines of intersection of the sub-grain boundaries where the decomposing unit is least co-ordinated with the lattice and progression of the reaction into the grains proceeds to a small depth up to $\sim$5% decomposition. During this period, eqn. (1) is applicable. With the more stable " monohydrate anhydride " however, this process continues up to 50% decomposition, but with the highly strained lattice of the trihydrate, cracks are propagated through the reactant after 5% decomposition in the manner envisaged by Prout and Tompkins,[3] thereby giving a branching mechanism which leads to the exponential expression given in eqn. (2). The smaller activation energy for decomposition of " trihydrate anhydride " is a consequence of the strain energy at the surfaces of the metastable phase. These investigations on *chemically* identical anhydrides emphasise how the topography of the reactant matrix largely determines the kinetics of the decomposition.

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[2] Young and Tompkins, *J.*, 1956, 3331.

[3] Prout and Tompkins, *Trans. Faraday Soc.*, 1944, **40**, 488.