647. *The Decomposition of Lead Styphnate Monohydrate.*

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The thermal decomposition of lead styphnate monohydrate proceeds smoothly between 195° and 229° with an activation energy of 33 kcal./mole. The mechanism of decomposition is similar to that previously proposed for barium styphnate monohydrate.

HAILES [1] found that large crystals of lead styphnate monohydrate decomposed smoothly between 200° and 228° with an activation energy of 46·7 kcal./mole according to an exponential expression consistent with the branching of linear reaction chains, but Garner, Gomm, and Hailes [2] analysed the decomposition plot according to a power law $p = ct^m$, where m varied between 0·88 and 4·43. More recently, Zingaro [3] measured the rate of dehydration of finely ground crystals of the monohydrate between 115° and 145°, and the present authors [4] investigated the dehydration and decomposition of the related compound, barium styphnate monohydrate. Conclusions differing from those of Hailes *et al.* were reached and the present paper extends our discussion [4] to the corresponding lead salt.

Experimental.—Regular, finely divided crystals of lead styphnate monohydrate, prepared from aqueous solution, were kindly supplied to us by Mr. G. W. C. Taylor. The crystals were not ground but passed through a 100-mesh B.S.S. sieve. The decomposition was carried out in an apparatus developed from a design by Thomas and Tompkins.[5]

Results and Discussion.—Small crystals of lead styphnate monohydrate decompose smoothly between 195° and 229°. Self-heating of the reactant becomes evident at 229° and above 235° the decomposition develops unfailingly into explosion. It was thus not possible, with this sample, to investigate the decomposition of a possible "hydrated" form as was done with large crystals of the barium salt at higher temperatures.[4] Typical plots of pressure against time are illustrated in Fig. 1; interruption of a run, as with the barium salt at low temperatures, introduced no new features. The point of inflection occurs at approximately 30% decomposition instead of at 50% for the barium salt, but the plots of the acceleratory period are approximately parabolic, as found with barium styphnate, and a suitable rate constant can be derived when the results are plotted as $p^{\frac{1}{2}}$ against t (Fig. 2). The complete kinetic expression is:

$$p = k(t - t_0)^2 \qquad (1)$$

where $t_0 \approx 10$ minutes and the activation energy calculated from the temperature coefficient of log $k^{\frac{1}{2}}$ is 33 kcal./mole, the corresponding figure for the barium salt being 36·5 kcal./mole. The reproducibility is better than ±2%.

Calculation from Zingaro's results shows that the dehydration of ground crystals proceeds with an activation energy of *ca.* 18 kcal./mole and would be largely complete at 200° within 7 minutes, *i.e.*, in a time shorter than that (20 minutes) required for the inception of the parabolic dependence at the same temperature. Since it was shown that the rates of dehydration of ground and of small crystals of barium styphnate monohydrate are approximately the same we conclude that the decomposition occurs also in the anhydrous regions of small crystals of the lead salt. Deviations from eqn. (1) are ascribed to the simultaneous occurrence of dehydration during the early stages of decomposition.

The only feature in which the decomposition plots for small crystals of the barium and the lead salt differ is that the sigmoid decomposition plot for lead styphnate is not symmetrical, the decay period having the characteristic form associated with decompositions of the "contracting-envelope" type.[6] The form of the plots obtained for small crystals,

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[1] Hailes, *Trans. Faraday Soc.*, 1933, **29**, 544.

[2] Garner, Gomm, and Hailes, *J.*, 1933, 1393.

[3] Zingaro, *J. Amer. Chem. Soc.*, 1954, **76**, 816.

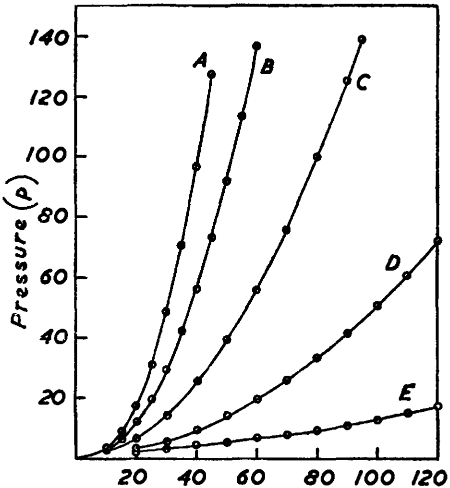
[4] Tompkins and Young, *Trans. Faraday Soc.*, 1956, **51**, in the press.

[5] Thomas and Tompkins, *Proc. Roy. Soc.*, 1951, *A*, **209**, 111.

[6] "Chemistry of the Solid State," ed. W. E. Garner, Butterworths, London, 1955.

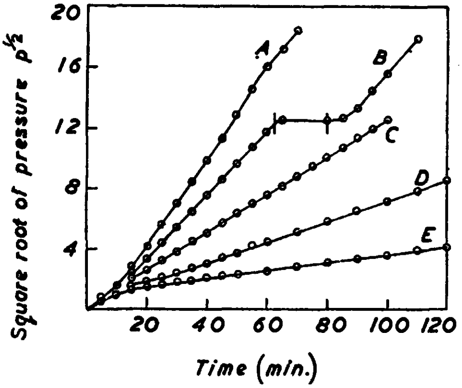
however, differs from those obtained by Garner *et al.* and by Hailes for large crystals, and the activation energies are different. It seems possible that with large single crystals the activation energy of 46·7 kcal./mole refers in part to the decomposition of the "hydrated" form since the corresponding value obtained by us for the "hydrated" barium salt was also high (52·6 kcal./mole). By analogy with the results for barium styphnate, which decomposes at similar rates with approximately the same activation energy and heat of decomposition, self-heating cannot provide the reason for higher value obtained by Hailes [1] below 229°. Since our activation energies for the barium and the lead salt differ by only 10% it is probable that the same primary process, the activation of an exposed or "surface" styphnate ion, is operative in each case.

FIG. 1. *The decomposition of lead styphnate monohydrate: pressure–time plots. The acceleratory period is approximately parabolic.*



A, 502·4° K. *B*, 497·5° K. *C*, 490·0° K. *D*, 487·6° K. *E*, 468·0° K.

FIG. 2. *The decomposition of lead styphnate monohydrate: (pressure)*$^{\frac{1}{2}}$ *plotted against time.*



A—E, as in Fig. 1.

Calculations using the geometrical methods described by Mampel [7] and by Jacobs and Tompkins [8] show that, since the maximum velocity occurs at 30% decomposition, the kinetics cannot be ascribed to either (i) initial increasing surface coverage by reaction product of all sub-grains nucleated simultaneously, followed by contraction of the interfaces thus created, since a parabolic acceleratory period would give a maximum rate below 10% decomposition, or (ii) nucleation, taking place according to a first-order law, of particles which decompose with a "contracting-envelope" interface, since this leads to a square-law dependence only to about 6% decomposition.

There seems, in fact, no reason to change the mechanism proposed for the decomposition of barium styphnate, *viz.*, nucleation of sub-grains at the edges and progression of the reaction into the grains with a non-coherent interface, the only difference being that the restriction of a predominantly faster rate of penetration of the reaction along one axis for the barium salt can be relaxed in the decomposition of lead styphnate.

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[7] Mampel, *Z. phys. Chem.*, 1940, **187**, *A*, 43, 235.
[8] Ref. 6, Chap. 7.