382. *The Thermal Decomposition of Lead Oxalate.*

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The kinetics of the decomposition of lead oxalate has been investigated at 309°, 325°, 335°, and 350°. The whole range of the decomposition is most adequately expressed by the equation $\log_e x/(1 - x) = kt + C$, where x is the fraction decomposed at the time t. The effect of fine grinding on the material is to remove any induction period and reduce slightly the acceleration period, as interference between chains commences sooner. Evidence is brought forward to show that the decomposition is probably catalysed by the solid products of the reaction. The energy of activation for both the accelerating and the decay period is 36 k.-cals.

A CONSIDERABLE amount of experimental work on the kinetics of the thermal decomposition of crystalline solids has been carried out and the general characteristics of the type of reaction Solid ⟶ Solid + Gas are now moderately well known. Bright and Garner (*J.*, 1934, 1872), Garner and Southon (*J.*, 1935, 1705), and Cooper and Garner (*Trans. Faraday Soc.*, 1936, **32**, 735) have demonstrated the formation of nuclei in the dehydration of salt hydrates and have studied their rates of growth. The decomposition of explosive solids such as lead azide (Garner and Gomm, *J.*, 1931, 2123) and mercury fulminate (Garner and Hailes, *Proc. Roy. Soc.*, 1933, *A*, **139**, 576) has also been investigated, and in order to explain some of the results Garner has put forward his " branching-chain theory " of solid decomposition. This theory has been criticised by MacDonald (*J.*, 1936, 832, 839) as the result of some work on the thermal decomposition of silver oxalate, mainly on the ground that decomposition along a network of lines of weakness in the crystal, *e.g.*, Smekal cracks, could only account for the decomposition of a small fraction of the whole solid. MacDonald put forward an alternative theory of planar nuclei to account for his results. Quite recently the branching theory has been extended by Prout and Tompkins (*Trans. Faraday Soc.*, 1944, **40**, 488) in a reinvestigation of the velocity of thermal decomposition of potassium permanganate and of silver permanganate (*ibid.*, 1946, **42**, 468). This theory probably provides a better physical basis for the branching theory and also takes into account the interference of the chains. The results embodied in the present communication are shown to be in general agreement with this theory. It has been shown (Bircumshaw and Harris, *J.*, 1939, 1637) that lead oxalate decomposes according to the equation $3Pb(OOC)_2 \longrightarrow 2PbO + Pb + 4CO_2 + 2CO$. The change is endothermic.

Experimental.

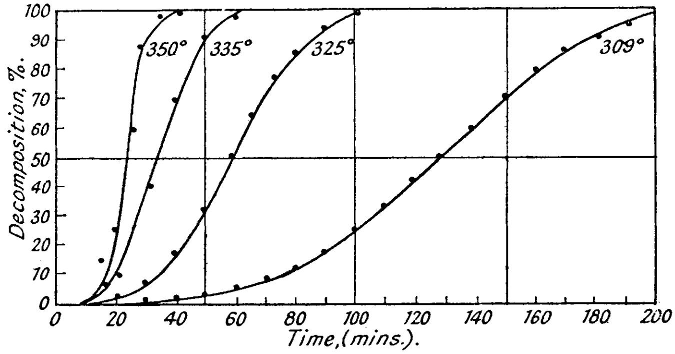
The lead oxalate used was prepared from " A.R. " reagents by precipitation from N/5-sodium oxalate solution with N/5-lead nitrate solution. Precipitation was carried out with boiling solutions and after filtration the precipitate was washed, dried at 100°, and stored in a vacuum desiccator.

The apparatus used for determining the rates consisted of a Pyrex-glass reaction tube connected to the usual pumping system consisting of a mercury diffusion pump backed by a Cenco pump. Pressure changes were measured with a McLeod gauge. Samples of the lead oxalate were placed in a small porcelain boat inside the reaction tube. The latter could be rapidly enclosed by a small electric tube furnace which was mounted on a " railway." The temperature was measured with a calibrated thermocouple placed inside the reaction tube. At suitable times the pumps were cut off, and the pressure allowed to rise for a given time (30 secs.). This rise gave the rate in arbitrary units which could be converted into suitable units (% decomp./min.) by graphical integration.

Results.—The plots of the fraction of lead oxalate decomposed against time (mins.) are shown in Fig. 1 and are of the usual sigmoid type. Four separate curves are given at temperatures 309°, 325°, 335°, and 350° respectively. The values of x, the fraction decomposed, were obtained by plotting the rate of decomposition measured in arbitrary pressure units against the time in minutes and integrating by square counting. The total area corresponds, of course, to 100% decomposition, and by dividing the area at any given time by the total area the fraction decomposed at this time was obtained. From these values the rates of decomposition can be expressed in percentage decomposed/min.

FIG. 1.

Decomposition of lead oxalate.



From these results the general validity of the well-known equations derived from the branching theory was examined :

$$\log_e x = kt + C \qquad (1)$$

$$\log_e (dx/dt) = kt + C \qquad (2)$$

In both cases a plot of log x or log dx/dt against time would give a straight line. This has been done (on semi-log paper) and it is seen that the equations hold almost up to the time of half decomposition (Figs. 2 and 3). The validity of the following equations has also been tested :

$$dx/dt = kt^m \qquad (3)$$

$$dx/dt = kx^{2/3} \qquad (4)$$

by plotting log dx/dt against log t and against log x. Both equations are deduced on the assumption that the reaction spreads spherically into the body of the solid. Garner has shown that the maximum value of m in equation (3) should be 3·0. In equation (4) the slope should of course be $\frac{2}{3}$. Neither equation holds in this case and it is concluded that the simple interface theory does not apply. Garner has found that the final stages in some solid decompositions (*e.g.*, of mercury fulminate) obey a unimolecular law, and this has been found to be the case over a limited range with lead oxalate.

The values at all four temperatures of the two constants (min.$^{-1}$) are given in Table I.

TABLE I.

Temp.	Unground $Pb(OOC)_2$.	Ground $Pb(OOC)_2$.	Temp.	Unground $Pb(OOC)_2$.	Ground $Pb(OOC)_2$.
Equation : $\log_e dx/dt = kt + C$.			Equation : $\log_e x = kt + C$.		
309°	$4·2 \times 10^{-2}$		309°	$6·5 \times 10^{-2}$	
325	$1·09 \times 10^{-1}$	$1·32 \times 10^{-1}$	325	$9·5 \times 10^{-2}$	$3·45 \times 10^{-1}$
335	$1·92 \times 10^{-1}$		335	$1·84 \times 10^{-1}$	
350	$2·43 \times 10^{-1}$		350	$2·4 \times 10^{-1}$	

In Fig. 6, the rate–time curves at 325° for lead oxalate, ground and unground, are compared. It will be seen that grinding removes practically the whole of the induction period, in this case 6—7 minutes.

The equations based on the simple branching theory appear to break down just before the maximum rate of decomposition is reached; one possible cause of this may be the interference of the chains, and this effect has been taken into account by Prout and Tompkins in discussing the results of their work on potassium and silver permanganates. They find that potassium permanganate decomposes according to the equation

$$\log_e x/(1 - x) = kt + C \qquad (5)$$

FIG. 2.

Plots of log x against time.

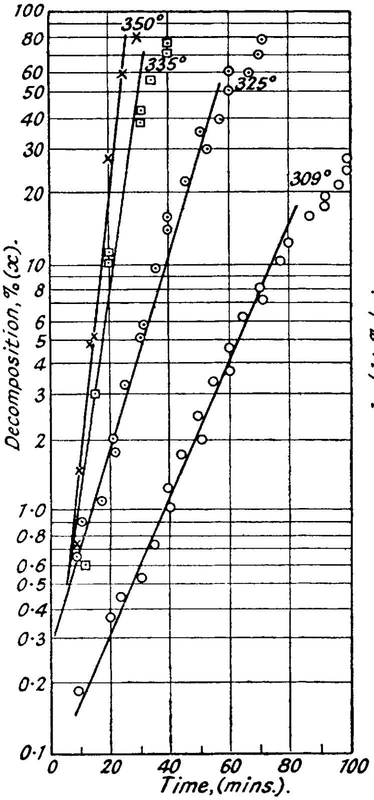


FIG. 3.

Plot of log d*x*/d*t against time.*

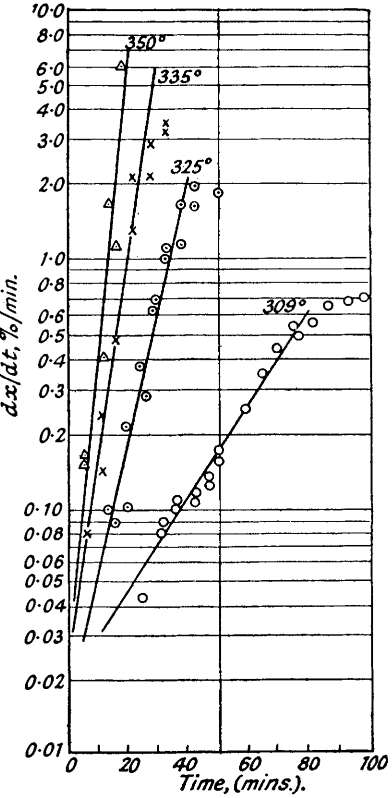
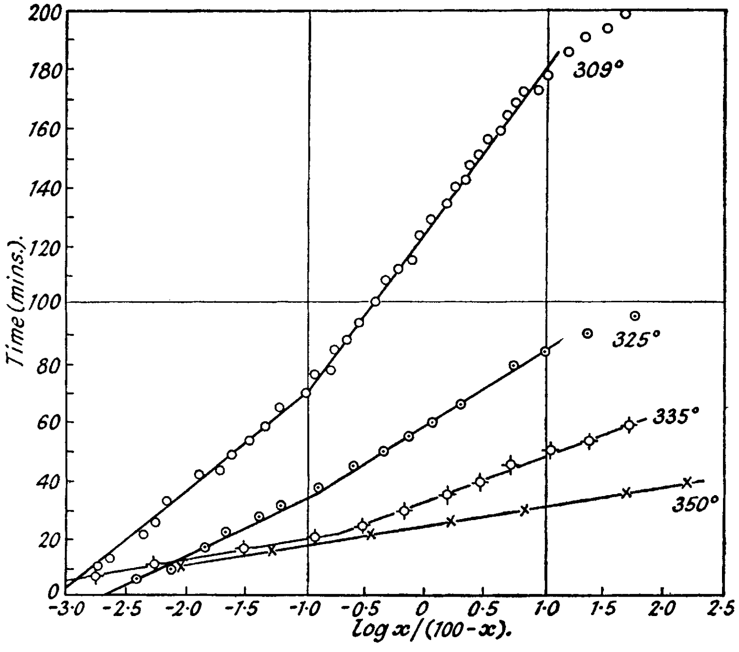


FIG. 4.

Plots of log x/(100 — *x*) *against time.*



where x is the fraction decomposed at the time t. To describe the complete course of the decomposition it is necessary to use two constants in the above equation owing to the fact that the sigmoid x–t curves are not symmetrical about the time for maximum rate of decomposition. In Fig. 4 are shown plots of $\log x/(1 - x)$ against t from which values of k for both the period of acceleration and the period of decay are obtained. The values are given in Table II.

TABLE II.

	Unground lead oxalate.		Ground lead oxalate.	
Temp.	k (accel.).	k (decay).	k (accel.).	k (decay).
309°	$6{\cdot}45 \times 10^{-2}$	$4{\cdot}15 \times 10^{-2}$		
325	$1{\cdot}73 \times 10^{-1}$	$9{\cdot}0 \times 10^{-2}$	$2{\cdot}09 \times 10^{-1}$	$7{\cdot}81 \times 10^{-2}$
335	$2{\cdot}83 \times 10^{-1}$	$1{\cdot}45 \times 10^{-1}$		
350	$4{\cdot}02 \times 10^{-1}$	$3{\cdot}15 \times 10^{-1}$		

Energy of activation. In Fig. 5 values of $\log k$ taken from Table II are plotted against $1/T$, where T is the absolute temperature. From the slopes of the graphs E is found to be 36,000 cals. for both the acceleration and the decay periods.

FIG. 5.

Energy of activation.

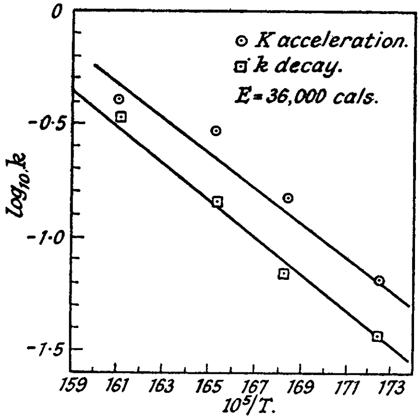
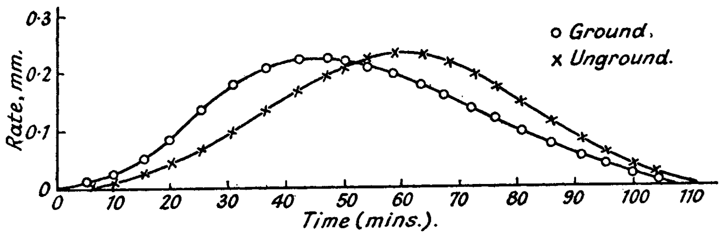


FIG. 6.

Comparison of rate–time curves of ground and unground lead oxalate decomposed at 325°. *Excess of nitrate ion.*



DISCUSSION.

There is abundant evidence that thermal decomposition in crystalline solids commences from nuclei, the formation and growth of which has in some cases been observed and photographed. The simple equations (3) and (4), which have been deduced on the assumption that the nucleus grows uniformly into the crystal, do not hold in the present case and it is necessary to assume some type of chain mechanism to account for the rapid acceleration of the decomposition in the early stages of the reaction. Garner adopted the idea of a degenerate branching process, but the mathematical treatment given by Semenoff (" Chain Reactions," 1935) makes no distinction between an energy chain and a chain propagated by some intermediate catalyst, *i.e.*, an autocatalytic reaction. The theory put forward by Prout and Tomkins probably represents an advance on the previous chain theory and, moreover, accounts for the whole reaction by assuming that branching occurs as the result of lateral strains set up in the crystal. These are relieved by the formation of Smekal cracks along which decomposition is favoured and further cracking is produced by more strains caused by the decomposition. The reaction thus spreads deeper into the crystal. Equation (5) represents the course of the whole reaction; but in general two equations each with a different constant (k) will be necessary owing to the asymmetry of the p–t curves. Garner's branching theory might not be expected to hold when individual chains begin to interfere with each other, and this has been found to be the case in the present work. The branching equation begins to fail a little before the time of half decomposition is reached. Similar behaviour was reported by Garner and Hailes in their work on mercury fulminate. They showed also that the second half of the reaction, after the maximum rate had been reached, could be considered as an ordinary unimolecular reaction.

It was not found possible to prepare large crystals of lead oxalate and investigate their decomposition, but a study of the decomposition of the ground salt gives the expected results. The general effect is obviously to increase the initial number of nuclei and thus remove any induction period. The acceleration period is reduced in duration, and interference between the chains commences sooner. Grinding does not, however, produce any great difference in the values of the acceleratory constants.

In the decay period the rate-controlling factor becomes the number of decomposed lead oxalate molecules. The theory put forward by Prout and Tomkins for the decomposition of potassium permanganate indicates that equation (5) will be obeyed in the decay period if it is assumed that decomposition is favoured in those molecules which are adjacent to a molecule of the product. This is the case with lead oxalate; but the same authors have found that with silver permanganate the unimolecular equation $\log_e (P - p) = kt + C$, where P is the final pressure and p the pressure at time t, is more applicable in the decay period. This is in agreement with the experimental observation that the rate of decomposition is not accelerated by the end-products of the reaction; *i.e.*, the silver permanganate molecules decompose without the restriction that they must be adjacent to the product molecules.

In the present work, although there is no direct evidence of the effect of end-products, the good agreement of the results with equation (5) in the decay period would indicate that lead oxalate behaves in a similar way to potassium permanganate.

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