

598. *The Thermal Decomposition of α -Lead Azide.*

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The thermal decomposition of well-aged α -lead azide has been studied between 268 and 283°. After an initial limited first-order reaction with an activation energy of 29 kcal. mole⁻¹, which is ascribed to the decomposition of surface carbonate, the main acceleratory period commences and progresses according to a cubic expression

$$[\alpha - \alpha_1(t)]^{1/3} = k(t - t_0)$$

with an apparent activation energy of 56 kcal. mole⁻¹. This kinetic dependence is attributed to the formation around a time t_0 of a constant number of lead nuclei which grow at a constant rate. However, the temperature-dependence of t_0 , and the deviations at higher fractional decomposition below the values predicted by the simple cubic expression, suggest that the number of nuclei involved in the acceleratory reaction increases with decomposition temperature, such that the true value for the activation energy of the interfacial reaction is 50 kcal. mole⁻¹.

THE thermal decomposition of α -lead azide had not been extensively studied until recently, owing to difficulties in obtaining preparations which behave reproducibly. However, it is now known that microcrystalline α -lead azide is readily hydrolysed in the laboratory atmosphere, forming basic azides and carbonates on the surface.¹⁻³ The decomposition of these surface compound affects the real course of the main decomposition in only minor respects, but can have an important influence on the results of the kinetic analysis of the acceleratory period, when it is carried out by conventional methods.

In 1931, Garner and Gomm⁴ studied the decomposition *in vacuo* of single crystals (2.4 mg.) between 200° and 300°. A contracting-envelope expression could be applied after a short acceleratory period, the correctness of this analysis being confirmed by the appearance of partially decomposed crystals which showed a white undecomposed core surrounded by a black sheath of lead. Using the technique of interrupted runs, a value of 47.6 kcal. mole⁻¹ was obtained for the activation energy of interfacial advance.

¹ Reitzner, *J. Phys. Chem.*, 1961, **65**, 948.

² Stammer, Abel, and Kaufmann, 1960, *Nature*, **185**, 456.

³ Feitknecht and Sahli, *Helv. Chim. Acta*, 1954, **37**, 1423.

⁴ Garner and Gomm, *J.*, 1931, 2123.

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Griffiths and Grocock⁵ in 1957 investigated the decomposition of pure, well-aged, microcrystalline α -lead azide by the technique of direct rate-measurement between 262 and 297°. The preparation used, consisting of single crystals $45 \times 35 \times 35 \mu$ in size, was remarkable for its narrow particle-size distribution. The main acceleratory period was analysed by means of logarithmic methods, and appeared to give a fifth-power dependence of fractional decomposition on time. A series of activation energies was obtained from these data, but one notes particularly that the value obtained from the maximum rate is 46.6 kcal. mole⁻¹, slightly lower than the result of Garner and Gomm. An initial, limited reaction was also observed, which appeared to have an activation energy of ca. 15 kcal. mole⁻¹. The explicit assumption was therefore made that the initial and main reactions could be treated independently. The decay period was analysed by use of a contracting-envelope expression.

More recently, Jach⁶ has described the kinetics of decomposition, between 195 and 253°, of microcrystalline α -lead azide with a particle-size distribution ranging from 7 to 40 μ . Consistent with this broad distribution, the decay period obeyed a first-order expression, but the acceleratory period, with which the present paper is concerned, was more complex. Thus, Jach reported an initial deceleratory reaction some 3–4% in extent, which he replaced by two disposable constants α_0 and t_0 , used to straighten a plot of $\ln(\alpha - \alpha_0)$ vs. $\ln(t - t_0)$. This procedure yields self-consistent sets of constants α_0 , t_0 and the slope, n , of the logarithmic plot, the choice of the best set being largely arbitrary. The choice of topochemical mechanism is determined by the value of the constant n . Selecting the slope $n = 2.2$ as a guide (ref. 6; Fig. 2), Jach analysed the acceleratory period according to the expression

$$\alpha - \alpha_0 = k(t - t_0)^2 \text{ for } 0.04 < \alpha < 0.24 \quad (1)$$

The quality of the fit is not perfect, the curvature of this function appearing to be too slight (ref. 6; Fig. 1).

There seems to be general agreement that the acceleratory period for this decomposition is not exponential in form; thus, in order to test the view that an analysis according to the alternative expression

$$[\alpha - \alpha_1(t)]^{1/n} = k(t - t_0) \quad (2)$$

(where $\alpha_1(t)$ represents the initial reaction presumed to continue throughout the acceleratory period) would lead to a more certain identification of the kinetic form, some unpublished results have been re-analysed by the technique of run-superimposition, the value of this technique having been tested by Haynes and Young⁷ with the simpler case of silver oxalate, and by Dominey *et al.*⁸ for the more complicated case of nickel oxalate.

EXPERIMENTAL AND RESULTS

The decomposition reaction was studied in a high-vacuum apparatus by the accumulatory method between 268 and 283°, using material which was nominally identical with that studied by Griffiths and Grocock.⁵ The apparatus included a vapour-trap which could be cooled either to -78° or to -196° , with a McLeod gauge for pressure measurements.

Two batches of azide were available. One, prepared in 1951, was four years old when it was decomposed; it had been stored in the laboratory atmosphere. The other was prepared in 1955 in identical fashion, and was supplied by the courtesy of G. W. C. Taylor of E.R.D.E., Waltham Abbey. It was stored in a vacuum desiccator containing phosphorus pentoxide, and was about two months old when decomposed. These materials are referred to as "aged" and "fresh," respectively; most of the work was done on the aged preparation.

Aged Material (Trap Temperature -78°).—In Fig. 1 are illustrated six decomposition runs on

⁵ Griffiths and Grocock, *J.*, 1957, 3380.

⁶ Jach, *Trans. Faraday Soc.*, 1963, 59, 947.

⁷ Haynes and Young, *Discuss. Faraday Soc.*, 1961, 31, 229.

⁸ Dominey, Morley, and Young, unpublished results.

material which had been aged for four years. The decay period is not illustrated, but in agreement with Garner and Gomm⁴ and with Griffiths and Grocock,⁵ it could be analysed according to a contracting-sphere expression, giving an activation energy of 50 ± 2 kcal. mole⁻¹. Apart from this activation energy, it is of no further interest.

It will be noticed that in each case the acceleratory period is preceded by an initial deceleratory evolution of gas which appears to be limited in extent to about $\alpha = 0.02$.

Aged Material (Trap Temperature -196°).—If, however, the decomposition is carried out at 271° with the vapour-trap cooled in liquid nitrogen, it is observed, as recorded in Fig. 2(a), that the initial deceleratory reaction can no longer be observed by means of its gas evolution, but that the acceleratory portion of the main reaction is unaffected, within experimental error. This finding is consistent with the view that the initial reaction concerns the decomposition of a carbonate on the surface of the aged preparation, the carbon dioxide evolved being measurable at -78° , yet condensed at -196° .

Fresh, Dried Material.—The view that hydrolysis by adsorbed moisture, and subsequent absorption of atmospheric carbon dioxide, is responsible for the surface contamination is given some support by the decomposition of freshly prepared material which had been protected from atmospheric attack. As shown in Fig. 2(b), the decomposition at 271° is independent of the temperature of the vapour-trap. It reaches the same maximum rate as was found for aged material, but the whole decomposition curve is displaced to lower times.

Analysis of the Kinetic Data.—The method of analysis depends on the assumption that the initial, deceleratory reaction, whilst being limited in extent, continues independently of the main acceleratory reaction, at least until the inflexion point is reached. This is justified in part by a rather more detailed analysis of the decomposition of nickel oxalate,⁸ where it was shown that the initial reaction is well represented by a contracting-parabola expression, confirming the findings of Jacobs and Kureishy.⁹ In the case of nickel oxalate, decomposition runs at lower temperatures showed that the initial reaction was greater in extent (α_1) than could be observed at higher temperatures, owing to the onset of the acceleratory reaction. There was, therefore, reason to suppose that the initial reaction was distinct from the acceleratory reaction, even though the activation energies for the two regions were identical. In the case of α -lead azide, that section of the initial reaction which can be observed directly is well represented by a first-order expression. The aiming point of this expression is not reached before the onset of the acceleratory reaction, and the activation energies for the two reactions prove to be quite different. This suggests that the reactions can occur concurrently.

The initial reaction. First, a master curve was selected. This is the run at 275.3° , illustrated in Fig. 1. There being no reason to suppose that the total extent of the initial reaction is dependent on temperature, all the data in this region were superimposed on the master curve by a transformation f_1 along the time-axis. The transformation f_1 was used to determine the activation energy, E_{f_1} , for the initial reaction, and was, of course, quite independent of the detailed kinetic analysis which followed. The optimum transformation factors f_1 were determined first by superimposing the experimental curves at a fixed, low value of α_1 where the nature of the curve is unaffected by the acceleratory reaction. A value of $\alpha = 0.016$ was selected for this purpose. The values of f_1 so obtained were then checked by comparing initial slopes and by searching for systematic rotations of tangents to the curves about the crossing point at $\alpha = 0.016$. The result of this axis-reduction is plotted on an expanded scale in Fig. 3 as α vs. $f_1 t$, the solid line drawn through the experimental points being given by the expression

$$\alpha_1 = 0.0195 [1 - \exp(-0.072 f_1 t)] \quad (3)$$

The experimental data are fitted by this expression up to $\alpha \sim 0.018$, in which region the acceleratory reaction begins to interfere systematically.

The acceleratory reaction. Values of α_1 were then calculated for all experimental runs, using the given factor $f_1 t$ in expression (3), and these values were subtracted from α for all times up to the point of inflexion. Owing to the particular form of the first-order function, the time-dependence of this correction for the initial reaction becomes very small as the inflexion point is approached, *i.e.*, it is equivalent to subtraction of an α_0 term at higher values of time. This is a simplification which was absent in the case of nickel oxalate.

The values of $[\alpha - \alpha_1(t)]$ so obtained were then analysed as a function of t , the original

⁹ Jacobs and Kureishy, *Trans. Faraday Soc.*, 1962, **58**, 551.

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measured experimental time. Several functions were tried, but the only one which was at all promising was the cube function

$$[\alpha - \alpha_1(t)]^{1/3} = k(t - t_0) \quad (4)$$

From plots of $[\alpha - \alpha_1(t)]^{1/3}$ vs. t , values of $t_0 (> 0)$ were obtained by extrapolation, and values of f_c , the transformation factor required to adjust the slopes of all the curves to the slope of the master curve (275.3°), were calculated.

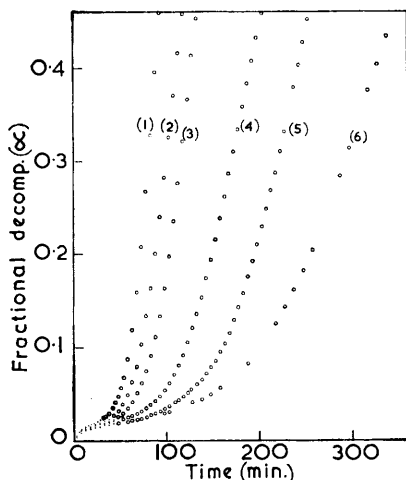


FIG. 1. The isothermal decomposition of aged α -lead azide plotted as fractional decomposition (α) against time. The vapour-trap temperature was -78° and the decomposition temperatures were: (1) 283.2° ; (2) 281.0° ; (3) 279.4° ; (4) 275.3° (master curve); (5) 271.5° ; and (6) 267.9° .

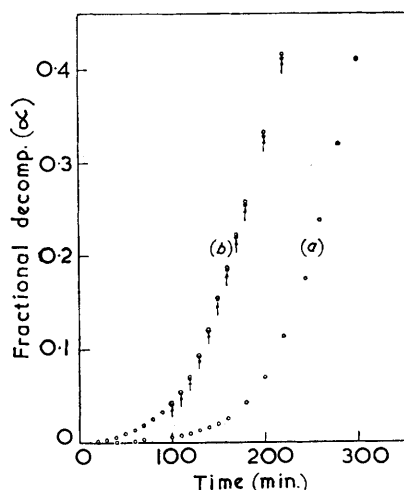


FIG. 2. (a) the isothermal decomposition of aged α -lead azide at 271° , plotted as fractional decomposition (α) against time, with the vapour-trap at -196° . The abscissa has been displaced to the right by 40 min., for clarity. (b) The isothermal decomposition of freshly prepared, dried α -lead azide at 271° , with the vapour-trap held at -78° (O) and at -196° (indicated by arrows).

The data were then translated through t_0 to the origin of the graph, the slopes transformed by f_c to the common (master) value and plotted as $\alpha - \alpha_1(t)$ vs. $f_c(t - t_0)$ (Fig. 4, where it can be seen that superimposition up to $\alpha \sim 0.3$ is obtained). The solid line drawn through these points is given by the expression

$$\alpha - \alpha_1(t) = 1.005 \times 10^{-7} [f_c(t - t_0)]^3 \quad (5)$$

The slight positive deviations which occur between 20 and 60 min. are commonly observed, and are believed to arise from a narrow distribution of t_0 -values within the specimen. This question will be discussed in a future Paper.¹⁰

The translation and transformation factors f_1 , t_0 , and f_c , and the quantity $\alpha_1(t_0)$, defined as the extent of the initial reaction at the onset (t_0) of the acceleratory reaction, are listed in the Table,

Temp.	f_1	t_0	$\alpha_1(t_0)$	f_c	Activation energies (in kcal. mole ⁻¹)
283.2°	1.413	20.8	0.0186	2.258	$E_{f_1} = 29 \pm 1$
281	1.178	22.2	0.0175	1.828	$E_{t_0} = 23 \pm 1$
279.4	1.009	23.8	0.0169	1.509	$E_{f_c} = 56 \pm 1$
275.3	1.00	29.0	0.0179	1.00	$E_{\alpha_1(t_0)} = 6 \pm 1$
271.5	0.723	31.9	0.0165	0.750	E (decay) = 50 ± 2
267.9	0.675	—	0.0156	0.531	E (max. rate) = 51 ± 2

¹⁰ Young, unpublished results.

together with the activation energies E_{f_1} , E_{t_0} , E_{f_c} , and $E_{\alpha_1(t_0)}$. The activation energies for the decay period and the maximum rate are included for comparison.

Deviations from the cube law. At fractional decompositions greater than 0.3, systematic deviations below the cubic expression begin to appear. These deviations would probably have escaped notice if the runs had been analysed individually without superimposition. This is

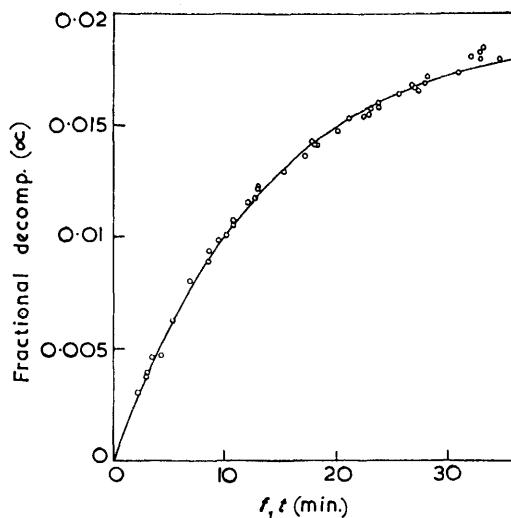


FIG. 3. The initial reaction, α_1 , as a function of $f_1 t$, where f_1 is the transformation factor. Data from the six runs illustrated in Fig. 1 are superimposed, and are represented by the solid line given by $\alpha_1 = 0.0195 [1 - \exp(-0.072 f_1 t)]$.

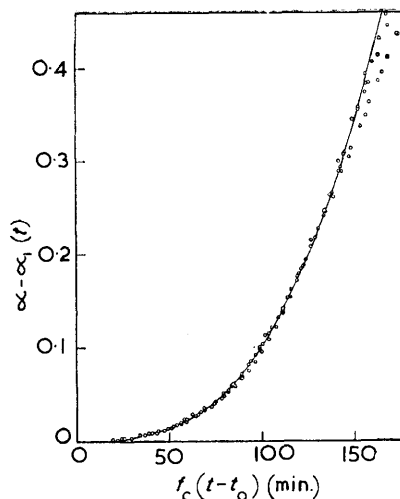


FIG. 4. The main acceleratory period of the decomposition of aged α -lead azide, plotted as $\alpha - \alpha_1(t)$ vs. $f_c(t - t_0)$, where f_c is the cubic transformation factor and t_0 is the effective time for commencement of nucleus development. Data points from the runs illustrated in Fig. 1 have been superimposed on the solid line given by $\alpha - \alpha_1(t) = 1.005 \times 10^{-7} [f_c(t - t_0)]^3$. About 80 overlapping data points have been omitted for clarity. The negative deviations at $\alpha > 0.3$ are greatest for the runs carried out at the highest temperatures.

one of the benefits of this analytical technique. In the present case, the deviation below the theoretical curve is most pronounced for those runs which were carried out at the highest temperature, in contrast with nickel oxalate where the reverse was observed. Such deviations denote earlier coalescence of reaction nuclei. Note, however, that the point of inflexion is not a function of temperature; it occurs at $\alpha \sim 0.46$.

DISCUSSION

The kinetic data for the isothermal decomposition of dried, freshly prepared α -lead azide can be analysed approximately by means of a simple cubic expression $\alpha = kt^3$, with no α_0 , t_0 corrections, though the derived plot does show signs of the "snaking" phenomena discussed elsewhere.¹⁰ The important points are that nucleation occurs at zero time and that the number of nuclei is approximately constant.

On storage in the laboratory atmosphere, an initial deceleratory reaction, ascribed to the decomposition of surface carbonate, develops, and the formation of active growth-nuclei required for the main acceleratory reaction is correspondingly delayed by a period t_0 , whether the gaseous products of the initial reaction are condensed or not. The rate of the

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acceleratory reaction is unaffected by storage; thus as far as the overall decomposition is concerned, the role of the surface carbonate appears to be simply the retardation of nucleus-formation.

On a simple model, one would expect nucleation to occur at a specific stage of the initial decomposition reaction, in which event the temperature-coefficient of $\alpha_1(t_0)$ would be zero and an activation energy of 29 kcal. mole⁻¹ would be obtained from t_0 . However, in practice, $\alpha_1(t_0)$ increases slightly as the decomposition temperature is raised, and the activation energy calculated from t_0 suffers a concomitant reduction. Although the reasons for this behaviour are obscure, it is evident either that the number of nuclei involved in the acceleratory reaction increases as $\alpha_1(t_0)$ increases, or that more material is available at t_0 for incorporation into a constant, topochemically determined number of germ-nuclei. The former alternative is preferred for the following reasons. First, as the decomposition temperature is increased, t_0 becomes larger than would be expected on the simple model. This is not consistent with the formation of larger, more active germ-nuclei. Secondly, those acceleratory periods which deviate first below the ideal cube law show the largest values of $\alpha_1(t_0)$. This deviation arises from nucleus-coalescence; thus one must assume that the number of active growth-nuclei does increase with decomposition temperature. The simplest assumption is that the temperature-dependence of the nucleus population is the same as that of $\alpha_1(t_0)$. Accordingly, one concludes that the rate constant, k , in the expression $[\alpha - \alpha_1(t)]^{1/3} = k(t - t_0)$, includes the factors $\exp[-E_{\alpha_1(t_0)}/RT]$ and $\exp[-E_{\text{interface}}/RT]$, whence $E_{\text{interface}} = 56 - 6 = 50$ kcal. mole⁻¹, to be compared with 50 kcal. mole⁻¹ for the decay period and 47.6 kcal. mole⁻¹ from the work of Garner and Gomm.⁴ The fact that the activation energy for the maximum rate is also similar, suggests that the earlier onset of nucleus-coalescence at the higher temperatures does not affect the nett area of the interface at coalescence. Calculations indicate that a 5% increase in nucleus population can reduce the range of validity of the cube law to $\alpha < 0.3$ if the nuclei are arranged in rows, *e.g.*, along surface fissures.

The positive deviations above the cube-law relationship between 20 and 60 min. are real, though smaller than when a fixed value, $\alpha_0 = 0.018$, is used instead of $\alpha_1(t)$. This is an indication that nucleation actually occurs in a narrow band of values around t_0 .¹⁰ Germ-nuclei on the low-time side of this distribution form with a marginally lower activation energy than nuclei on the high-time side. As the decomposition temperature is raised, more of the spectrum is traversed by the activation function; thus at the higher temperature, more nuclei form.

The origin of this distribution is not known, but one should note that the mere uncovering of potential nucleus-forming sites is not sufficient to account for the temperature-coefficient of nucleus population. Infection must also occur. Either lead atoms must diffuse to these sites, or electrons, thermally released from, say, electron donors produced by the initial reaction, must be trapped there. Both processes are likely to be activated. These general concepts are given some support by the known catalytic effect of electron donors introduced on to the crystal surface,¹¹ and by the aggregation of metal atoms adsorbed on crystal surfaces,¹² though one cannot distinguish between alternative mechanism on the present evidence.

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¹¹ Reitzner, Kaufmann, and Bartell, *J. Phys. Chem.*, 1962, **66**, 421.

¹² Camp, Deb, Evans, Montagu-Pollock, and Yoffe, "Reactivity of Solids," ed. J. H. de Boer, Elsevier, Amsterdam, 1961, p. 321.