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The Thermal Decomposition of Irradiated α Lead Azide*

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ABSTRACT

The thermal decomposition of unirradiated and heavily reactor irradiated colloidal α - PbN_6 has been studied in the temperature range 195°C - 253°C and 173°C - 239°C respectively. The irradiation vastly reduces the induction and acceleratory periods found with unirradiated material and increases the maximum rate and the rate of the final decay. The maximum rate normally occurs at about 40% decomposition but is shifted to approximately zero time on irradiation. The change in decay rate on irradiation is demonstrated by the two rate constants for decay,

$$k \text{ (unirradiated)} = 10^{12.0 \pm 1.0} \exp(-36.3 \pm 2.3\text{kc/m/RT}) \text{ and}$$

$$k \text{ (irradiated)} = 10^{7.9 \pm 1.0} \exp(-25.7 \pm 2.4\text{kc/m/RT}). \text{ The}$$

significant drop in activation energy is possibly associated with changes in electronic excitation energies, while the drop in frequency factor is thought to result from gross structural changes accompanying the irradiation. The power laws observed in the acceleratory region are interpreted in terms of simultaneous surface and 3-dimensional reactions.

The thermal decomposition of α PbN_6 has been the object of a few studies since 1933. Garner and Gomm⁽¹⁾ first investigated the decomposition of small single crystals and found the reaction to obey a contracting envelope type of mechanism. Partially decomposed crystals when broken open, revealed a white undecomposed core surrounded by a black cover of lead. Later in 1933, Garner et al⁽²⁾ concluded that the acceleratory stage of the reaction was governed by a power law between linear and cubic. This they attributed to "normal growth" as opposed to branching which would have resulted in much higher values of the power. No subsequent investigations were conducted until 1957 when Griffiths and Grocock⁽³⁾ reported an extensive investigation of the decomposition using a new technique. Many of their results confirmed the earlier conclusions of Garner et al but they went further. They concluded that nucleation occurred on external surfaces at a rate proportional to time and decomposition caused these to grow three dimensionally into the crystal. They offered an explanation of nucleus formation and decomposition growth in terms of positive hole production. Grocock⁽⁴⁾ then studied the effect of various irradiations on the subsequent thermal decomposition but no definite conclusions were reached as regards irradiation effects.

More recently, a group of workers at Picatinny Arsenal have investigated the decomposition. Stamler, Abel and Kaufman⁽⁵⁾ using thermogravimetric and X-ray techniques found evidence for a step-wise decomposition corresponding to different phases of PbN_6 .

The object of the current investigation is to further understand

this decomposition especially in terms of irradiation effects. The drop in activation energy on irradiation reported by Grocock⁽⁴⁾ is indeed thought provoking. It was felt that this observation should perhaps be extended further in that it represents an effect not generally expected. The author believes that the power laws deduced by Griffiths and Grocock⁽³⁾ for unirradiated material are perhaps open to question. The general problem of the effect of irradiation on thermal decomposition is, however, the most intriguing one and it is mainly in an attempt to further understand this ill-understood subject that the present work was conducted. This effect has received very little attention. In addition to the work of Griffiths and Grocock mentioned above, some other studies include the effect of fission product recoils on the subsequent decomposition of Uranyl Oxalate by Young⁽⁹⁾ in which an interesting topological effect was observed. Decomposition appeared to occur around fission tracks resulting in expanding cylinders. Flanagan⁽¹⁹⁾ studied the decomposition of lead styphnate monohydrate with respect to γ -ray and neutron irradiation effects. He found γ -rays to be ineffective but the neutron irradiation appeared to provide many more nuclei from which decomposition could proceed, thus increasing the rates of decomposition. From a series of studies involving various irradiations on permanganates by Prout⁽¹⁸⁾, it was concluded that extensive cracking occurs in irradiated crystals resulting from decomposition centers caused by preferential annealing and Wigner energy releases around point defects. However, the whole subject requires much more work, even on an elementary level.

This is a preliminary study using colloidal α PbN_6 . The effect of irradiation on larger crystals and perhaps single crystals will be reported at a later date.

EXPERIMENTAL

The reaction $\text{PbN}_6 \longrightarrow \text{Pb} + 3\text{N}_2$ was followed by pressure measurement in a closed system. A colloidal type of α PbN_6 was obtained from Picatinny Arsenal and was used without any further processing. The average particle size was 7μ but ranged from 40μ down to an unknown minimum but one quoted as being very small. Approximately 5 mg portions were dried for 3 hours at 80°C and encapsulated under backing pump vacuum into quartz vials. Some of the vials were irradiated simultaneously in the Brookhaven reactor. The reaction vessel was a horizontal quartz tube with a flat one inch depression in the middle and was heated by a furnace controlled to $\pm 0.1^\circ\text{C}$. The samples (whether irradiated or not) were emptied from the vials into a platinum bucket attached to a magnetically operated device which allowed the crystals to be introduced into the depression after evacuation. Reactions therefore took place on a surface of lead left by previous reactions. This was shown to be reproducible with respect to a bare quartz surface. Pressures were measured by a Pirani gauge whose signal was recorded continuously on a pre-calibrated West recorder. The final pressure never exceeded 150μ . In low temperature runs, final pressures were obtained by deliberately raising the temperature. This procedure was adopted for all the runs but at the higher temperatures no additional pressure release was observed.

RESULTS

The decomposition of unirradiated material was studied in the temperature range 195°C - 253°C and irradiated material in the range 173°C - 239°C. It was decided that a heavy irradiation dose might yield more information in this preliminary study. The samples were irradiated for 35 hours in the Brookhaven reactor in a facility quoted as having a flux of approximately $7 \text{ to } 8 \times 10^{12}$ neutrons/cm²/sec of which approximately 2×10^{11} were epi-Cd.

A typical α/t plot for unirradiated material is shown in Fig. 1, where α is the fraction of the total decomposition. The closed circles represent the experimental points for unirradiated material. An induction period is observed followed by an acceleratory, maximum rate and decay stage. Sometimes near the beginning of the reaction, a small acceleratory region similar to that observed by Griffiths and Grocock⁽³⁾ was seen but only in two or three cases. The period before the main acceleration is essentially linear with respect to time. The acceleratory region itself is fitted in the figure to an expression

$$(\alpha - \alpha_0) = a(t - t_0)^2 \quad (1)$$

represented by open triangles. The fit is good, but not perfect or unique. This point will be clarified later. After the maximum rate, the decomposition follows very closely an exponential decay of the form

$$\alpha = \alpha_{\infty} \left[1 - \exp \left\{ -k(t - t_0) \right\} \right] \quad (2)$$

shown in Fig. 1. as open squares and with $\alpha_{\infty} = 95\%$. The equation generally fits from about $\alpha = 50\%$ to above 90%.

Irradiation significantly alters the decomposition kinetics. Fig. 1 also shows an α/t plot for irradiated material at approximately the same temperature as the run on unirradiated material shown in the same figure. The open circles are the experimental points for irradiated material. The induction period is drastically reduced. It is actually difficult to detect the induction period in this figure but it is more clear on an expanded scale. The acceleratory period is virtually absent. There is a short initial gas evolution during the induction period but this amounts to less than 1% decomposition. After this the rate rises immediately to its maximum value and subsequently drops in the same way as the decay stage of the unirradiated material represented by equation 2. However, the fit shown as closed triangles in the figure does not extend to as high values of α as with unirradiated material.

Attempts were made to fit the main acceleratory region of the unirradiated material to exponential and power laws as well as the Prout-Tompkins equation. The most satisfactory fits were the power laws, $\alpha = at^m$, but even here various complications arose which are described now. Using the raw data shown in Fig. 1, a $\log \alpha / \log t$ plot gave two slopes as shown in Fig. 2 by the closed circles. The initial slope is near unity and the slope during the acceleratory region is 6.5. It thus seems likely that a reaction is predominating near the beginning of the decomposition which then stops or is overshadowed by the reaction

which makes up the main acceleratory region. It was then decided to try $\log \alpha / \log t$ plots with zero time corrections. Thus, $\log (\alpha - \alpha_0)$ was plotted against $\log (t - t_0)$ where t_0 is a zero time correction and α_0 is the corresponding value of α at time t_0 . The choice of the point α_0, t_0 is arbitrary but was chosen as reasonably close to the acceleratory period as possible. The values of α_0 were in general not far from 4%. The "corrected" plot is shown in Fig. 2 as open circles. It has a slope of 2.2 in the region where the uncorrected plot showed a 6.5 slope. The important fact that emerges is that the slope corresponding to the acceleratory region is very critically dependent on the correction. Here is a clear demonstration of the danger of drawing too rigid conclusions from power laws. This dependence of the power on the correction is shown in table I. In each case there was a good straight line over a substantial portion of the run. The same general features were obtained with all the runs (at different temperatures) on unirradiated material. The slopes corresponding to the acceleratory period varied from 2.7 to 7.2 for the uncorrected plots to a value very close to 2 for plots having the correction. This is shown in table II. The average value of 5.1 for the uncorrected plots is in agreement with Griffiths and Groococks' observation. They obtained a slope of 4 for a $\log (d\alpha/dt)$ vs $\log t$ plot which is equivalent. The true value of n in the power law $\alpha = t^n$ is thus largely a matter of conjecture. All that can be said is that it is a low power (five or less).

It might be mentioned here that the irradiated material exploded when a temperature of 255.7°C was employed, as compared to an explosion

obtained at 258.3°C with the unirradiated material. Also, the explosion with the irradiated crystals was more intense. However, this irradiation effect was not examined any further since the explosions involved elaborate apparatus repairs and were in any case not the main purpose of this study.

Activation Energy Plots.

The following parameters were obtained from the α/t curves of the unirradiated material for subsequent Arrhenius plots:

- a) The induction period, τ , which is arbitrarily defined as the intercept on the time axis of an extrapolation of the maximum rate.
- b) The constant "a" of the equation

$$(\alpha - \alpha_0) = a(t - t_0)^2$$

which appears to hold over the acceleratory period. The method was to take 3 points well within this period and solve the equation analytically. This gave a double check on the values of α_0 and t_0 used for obtaining table II.

- c) The maximum rate itself, $k_{\max}$.
- d) The constant k in the equation

$$\alpha = \alpha_{\infty} \left[1 - \exp\{-k(t-t_0)\} \right]$$

which represents the decay rate. For irradiated material, the only parameters obtainable were those corresponding to a), c) and d). The

Arrhenius plots for $1/\tau$ (unirradiated) and $1/\tau$ (irradiated) are shown together in Fig. 3, $\sqrt{a}$ on Fig. 4, $k_{\max}$ (unirradiated) and $k_{\max}$ (irradiated) on Fig. 5 and k (unirradiated) and k (irradiated) on Fig. 6. The reason for using $\sqrt{a}$ instead of "a" in Fig. 4 is as follows: The square law itself is indicative of a two-dimensional reaction from a single nucleus, repeated in the real case at many nuclei. In this event, the activation energy sought is for the velocity of this growth, $v = v_0 e^{-E/RT}$. The area decomposed at time t is then proportional to $(vt)^2$ and therefore α is proportional to $v^2 t^2$ where v^2 is proportional to the quantity "a". An Arrhenius plot of "a" itself will then yield $2E$ and one of $\sqrt{a}$ will yield E . This argument can, of course, be extended to three dimensions where, if the acceleratory region had fitted $\alpha = at^3$ more closely, the activation energy for the fundamental step, i.e. velocity of penetration from a single point, would be given by an Arrhenius plot of $\sqrt[3]{a}$. As implied previously, the author believes that to single out any power such as 2 or 3 is arbitrary, but it serves the purpose of indicating what the approximate activation energy is for the fundamental step in the acceleratory region.

The following features of the Arrhenius plots should be noted. From Fig. 3 it is evident that the defined induction period τ is not simple and is probably influenced over the temperature range studied by two or more concurrent events, whether the material is irradiated or not. The maximum rates give straight line plots but irradiation results in a marked decrease in the activation energy and pre-exponential factor. The same remarks can be made for the plots of k (irradiated) and k (unirradiated). The latter quantities are represented by the following:

$$k \text{ (unirradiated)} = 10^{12.0 \pm 1.0} \exp(-36.3 \pm 2.3 \text{ kcal/m/RT}) \quad (4)$$

$$k \text{ (irradiated)} = 10^{7.9 \pm 1.0} \exp(-25.7 \pm 2.4 \text{ kcal/m/RT}) \quad (5)$$

The overall rates in the temperature region studied are increased over the whole decomposition range. Note: the errors quoted are the statistical probable errors and do not include experimental errors. Grocock (4) also observed a marked decrease in activation energy on X-ray and pile irradiation. The activation energy for irradiated materials obtained by him agrees closely with that quoted here but his value for unirradiated material is a little higher.

The final pressures obtained for all runs on the unirradiated samples correspond, on the average, to almost total theoretical decomposition. With irradiated samples however, the final pressure/weight ratios were about 20% lower than unirradiated. It is most reasonable to assume that the irradiation decomposition amounted to approximately 20%. The irradiated crystals were completely black as compared to an off-white color for the unirradiated crystals.

Before going on to the discussion, an interesting phenomenon in this decomposition might be mentioned in passing. At very low temperatures, where experimentally the times involved are too long for a complete decomposition to be studied, the initial linear period preceding the acceleratory region is found to extend to quite high α (30%). At the lowest temperature studied, this took 2 weeks to attain. This percentage decomposition (30%) at higher temperatures represents a region

well within the acceleratory period and is almost at the maximum rate. It might be mentioned that a very similar phenomenon was observed on a totally different decomposition, that of NaBrO_3 ⁽⁶⁾. Tentatively, it may be suggested that as very low temperatures are attained, only those processes occurring with very low activation energy such as decomposition along dislocation lines, etc. are fast enough to be observed and that at higher temperatures they are soon masked by nucleation and normal growth, both of which have higher activation energies. However, this will be the subject of a later paper.

DISCUSSION

1. Topochemical aspects of the reaction

a. Unirradiated material. The initial stages of the reaction exhibit complexities, but basically it follows a linear rate and has an activation energy somewhat lower than the remainder of the reaction. It is only possible to guess what this means. Griffiths and Grocock⁽³⁾ suggest that basic lead carbonates are decomposing before the main reaction begins. It is also possible that initially reaction occurs preferentially at surfaces, cracks, dislocations, etc. The linearity of the rate and the low activation energy tend to support the latter idea. The true answer probably involves all or most of these suggestions. At higher temperatures, these initial events are somewhat overshadowed by the reactions of higher activation energy, and the induction periods become relatively shorter. As a result, the Arrhenius plot for $1/t$ tends to swing upwards from the

straight line at higher temperatures.

In the acceleratory region, the complexity of the $\log \alpha$ vs $\log t$ plots makes it rather doubtful that any exact conclusions can be reached regarding the topochemical details of the reaction. In the work of Griffiths and Grocock already referred to, it was concluded that the rate of nucleus formation was proportional to the first power of the time. This conclusion was arrived at on the basis of a value of 4 for the slope of the $\log d\alpha/dt$ vs $\log t$ plots, together with the assumption that the growth contributes a t^3 factor to t^m . They did not make any zero time corrections in their plots and it is conceivable that the true value of m is perhaps less than 4. Retaining the same assumption for a t^3 growth law, the nucleation rate might then be proportional to a power of t anywhere from zero to one. Therefore, in view of the initial complexities in this reaction, the author regards the conclusion of a nucleation rate proportional to t as perhaps too simple a picture.

The acceleratory period appears to correspond best to a power law $\alpha = at^m$. There is doubt as to the exact value of m , but it can definitely be stated to be in the region 2 to 5, although when t_0 , α_0 corrections are made, it appears to be between 2 and 3. It should be noted that for a reaction occurring only the surface, the power should theoretically be 2 and for one occurring only 3-dimensionally, it should be 3. This applies to non-interfering growths which is normally true at the beginning of the reaction. If the activation energy for nucleus formation is not too high, so that enough nuclei form during this growth period, the power will be higher depending on the rate law for nucleus formation.

It would not be safe to draw any rigid conclusions about the acceleratory region. However, there is some indication that a surface and a 3-dimensional reaction are occurring simultaneously. This would be true if their respective activation energies were not too different. Then if it is assumed that $E_{\text{surface}} < E_{\text{bulk}}$, the bulk reaction will gain predominance at higher temperatures. The value of α at which $d\alpha/dt$ max. occurs will be higher for a predominantly 3-dimensional reaction than for a surface one. For instance in the extreme case of a 3-dimensional reaction starting from one nucleus on the surface of a sphere, $(d\alpha/dt)_{\text{max}}$ theoretically occurs at the high value of $\alpha = 16/27 = 59.3\%$ ⁽⁷⁾. At the other extreme, if the surface reaction is instantaneous, and is followed by a 3-dimensional reaction, $(d\alpha/dt)_{\text{max}}$ occurs at $\alpha = 0$, this limiting case being, of course, the contracting envelope. Fig. 7 shows a plot of α_{max} which is the value of α at the maximum rate vs temperature. Clearly, α_{max} rises with temperature. This tends to support the idea that both 3-dimensional and surface reactions are occurring simultaneously and that the 3-dimensional reaction with the higher activation energy becomes relatively more important at higher temperatures. This is also consistent with the result that the corrected powers lie between 2 and 3, if it is assumed that the nucleus formation rate is low. Griffiths and Grocock did in fact find high activation energies for nucleus formation. It might be mentioned in passing that the powers quoted in this work could be lower than those of Griffith and Grocock because the crystals used here were smaller, so that the increased surface area would favor the lower power. But this would certainly not be enough to lower the value by as much as

3 or even 2.

The later stages of the reaction appear to follow a simple first order decay law. At this stage of the reaction one would expect that only 3-dimensional contracting envelope kinetics occurs, since all free surfaces would almost certainly have reacted at this stage. This is supported by microscopic observations of Garner et al⁽¹⁾ and Griffiths and Grocock⁽³⁾ who found that partially decomposed crystals show an inner core of virgin material surrounded with a layer of lead. However, such a contracting envelope in general is not expected to give a pure exponential decay although the insensitivity of curve fitting may not be sufficient to distinguish the exponential decay from the law governing the contracting envelope. Certain particle size distributions can lead to a pure exponential decay even though each particle is undergoing a contracting envelope mechanism. This is discussed later in connection with irradiation effects.

In the view of the author, it seems more appropriate not to draw any rigid conclusions as to the exact power laws or the detailed topochemical mechanisms. The question of nucleation rate probably cannot be solved by simple thermal decomposition techniques and a more sophisticated approach, such as direct observation of nuclei by electron-microscopy might answer the question as to whether nucleation is instantaneous or follows a power law or any other law. The techniques used to date on PbN_6 are almost certainly too insensitive.

Rather, a few general statements could be made as follows:

- a) The initial stages of the reaction might be a break-up of carbonates and/or such energetically favorable reactions as those on surfaces, cracks, dislocations, etc.
- b) The acceleratory period represents simultaneous surface and 3-dimensional penetration and possibly also further nucleation.
- c) The final decay is a continuation of the 3-dimensional penetration after coalescence of interfaces, the decay law being governed by such topochemical features as particle size distributions, etc.

Before passing on to a discussion of irradiation effects, brief mention might be made of one topochemical explanation of these results, viz cracking. If cracking occurs continuously throughout the reaction, one might suppose that this could result in sigmoidal behavior, an acceleration being due to a continuous increase in surface area and a decay being due to the reaction of an immense number of small single crystals incapable of further cracking. However, as attractive and simple an explanation as this is, it suffers in that the number n in the power law $\alpha = at^n$ would be very much higher than observed. Furthermore, cracking will not explain the vast drop accompanying irradiation in the value of α at which the maximum rate occurs. There is no doubt, however, that some cracking occurs at the beginning of the reaction.⁽⁸⁾

b. Irradiated materials. The effects of irradiation on the α/t plots are extremely marked. The induction period is drastically reduced, the acceleratory period is virtually non-existent and the reaction after the induction period essentially begins with its maximum rate. It appears likely that the explanation for such behavior is as follows: The induction period is normally associated with the simultaneous formation

and growth of nuclei. If it is postulated that the effect of irradiation is to vastly increase the number of such nuclei or potential nuclei, the delay in attaining the maximum rate must largely disappear. On reaching furnace temperature, a rapid surface reaction occurs from the points of nucleation and the reaction which follows is a simple 3-dimensional penetration of the interface. From the arguments presented later it seems feasible that the surface reaction is faster with irradiated material, aside from the larger number of points from which this reaction spreads.

2. The damaged state of PbN_6

Before discussing the effect of irradiation on the actual interface penetration rates, it is necessary to present some picture of the crystal after the heavy irradiation. The difficulty of presenting a physical picture of the damaged PbN_6 crystal is due entirely to a lack of experimental work in this field, especially for higher doses. To the knowledge of the author, the only substantial radiation chemistry studies involving particle radiation have been those of Young on uranyl oxalate⁽⁹⁾ and Hall and Walton on nitrates.⁽¹⁰⁾ Both workers find particle irradiation a much more efficient decomposing agent than photons. Some work has been done on low dose irradiation of PbN_6 where a lattice expansion was observed⁽¹¹⁾ and γ -ray and neutron irradiation of NaN_3 ⁽¹²⁾ in which pile irradiation caused more heavy locally damaged regions in a matrix of relatively undamaged crystal as compared to γ -ray irradiation which produced a more homogeneous type of damage. The final answer to the question must, therefore, await further experimental work, especially x-ray and electron microscope analysis of damaged PbN_6 .

However, one can, by analogy with existing radiation chemical knowledge of say nitrates, which have been extensively studied^(10, 13, 14, 15) form some crude physical picture of what the state of the crystal might be. Initially, the irradiation will produce N_2 at all surfaces, both internal and external, and at imperfections such as dislocations, etc. Further irradiation will then probably cause decomposition at normal lattice sites with build-up of gaseous N_2 internally. This will diffuse to pockets causing rupture and further decomposition at newly formed surfaces. Vacancies and/or clusters of vacancies will thus be left behind and Pb will accumulate at surfaces and at internal regions of the crystal. Most of the damage will be of a permanent type and will not be annealed out at the high temperature of the subsequent thermal decomposition. This may be especially true of PbN_6 which is expected to possess some covalent properties similar to AgN_3 so that simple relaxation of strain and damage will be less likely. The relatively undamaged parts of the crystal might even undergo a partial amorphisation under these strained conditions.

3. Change of interface penetration rate on irradiation

In view of the vastly changed shape of the curves on irradiation, it is difficult to find any parameters to compare in the two cases. One must constantly be aware of a qualitative change in the material itself, especially with a heavily irradiated and not completely ionic solid such as PbN_6 . Under these circumstances, changes in kinetics are to be expected. However, in the almost complete absence of any information regarding the heavily irradiated state of PbN_6 it is only possible to make intelligent

guesses about the parameters to be compared before and after irradiation and also about the interpretation of these changes.

In order to make any direct comparison of growth rates for unirradiated and irradiated material, the assumption is now made that the period immediately following the maximum rates represent the same reaction, i.e. the same microscopic chemical event and that in this region there are no more possible complicating effects of nucleation. This region, which can be represented by the equation

$$\alpha = \alpha_{\infty} \left[1 - \exp \left\{ -k(t - t_0) \right\} \right]$$

for both irradiated and unirradiated material can then be used to compare the growth rates. The quantities

$$k \text{ (unirradiated)} = 10^{12.0 \pm 1.0} \exp(-36.3 \pm 2.3 \text{ kcal/m/RT})$$

$$k \text{ (irradiated)} = 10^{7.9 \pm 1.0} \exp(-25.7 \pm 2.4 \text{ kcal/m/RT})$$

are assumed proportional to rate of advance of an interface. Although this seems intuitively obvious, an example is shown in Appendix I which demonstrates that this is so. Thus, irradiation effects two important changes:

- i) The activation energy for interface growth is markedly reduced.
- ii) The pre-exponential factor for interface growth is markedly reduced.

The drop in activation energy may be associated with a change in the excitation energy of the electrons. Such a change might easily result from the excessive local strain brought on by an irradiation decomposition of 20%. The appearance, on the average, of one vacancy or foreign body per 5 lattice points must introduce large local strains which are not annealed. These may certainly introduce electron traps sufficient to account for the observed drop in activation energy. The act of decomposition is then determined by the untrapping of these electrons. The drop in activation energy resulting from irradiation would in this case be due to the greater height of the traps after the straining with a consequently lower energy necessary for untrapping the electrons. However, the possibility must be borne in mind that after such heavy irradiation damage the entire structure of the crystal might be changed as is the case for certain of the more covalent types of crystals.⁽¹⁶⁾ PbN_6 is probably more akin to AgN_3 than say KN_3 or NaN_3 in the sense of having much more covalent character. Irradiation strains are not as easily removed by relaxation effects, and overall structural changes may result. Under these circumstances changes in electronic excitation energies may again be anticipated. However, the results of this investigation definitely cannot distinguish between a homogeneous change in crystal structure or a state represented by small, relatively undamaged regions in an amorphous matrix. Since the band structure is unknown, any statements as to excitation vs. positive hole formation is a compound of one guess upon another and would serve no useful purpose.

The change in the pre-exponential factor is even more difficult to interpret. This change appears to be related to a fundamental microscopic event rather than a change in topochemical structure (such as cracking for example) accompanying irradiation. The reader is referred to Appendix 11. An overall change in crystal structure could bring a change in frequency factor, although it is difficult to foresee a change of four orders of magnitude by such a means. A clue as to what might be happening is the possible presence of an open structure brought about by vacancy introduction on irradiation. If the currently accepted idea of reaction between two excitons or positive holes is accepted, then the presence of vacancies homogeneously distributed in large numbers would hinder the reaction between these two entities. A crude picture is that every 10^{-13} seconds these two entities will react if they have sufficient activation energy. The partial relaxation of azides into these vacancies could easily decrease this probability of reaction by three or four orders of magnitude. They would in fact be ^{partially} trapped by the vacancies. A probability factor, much the same as that introduced into bimolecular gas reactions might be operative, the increase of entropy in this case resulting from the presence of vacancies. This might be looked upon as a "cage effect" encountered in radiation chemical studies but the cage now hinders a reaction instead of helping. In the radiation decomposition of nitrates for example, the primary act of decomposition into $\text{NO}_2^{\text{rad}} + \text{O}$ is facilitated by the "free space" into which the O atom can vibrate. (13, 14)

SUMMARY

Lead azide tends to decompose by a contracting envelope mechanism from a fully nucleated surface. Nucleation and growth on the surface prevent immediate appearance of contracting envelope kinetics and give rise to sigmoidal behavior and a power law between square and cubic within the acceleratory region. Irradiation hastens nucleation and growth and results in the immediate appearance of a contracting envelope type of kinetics. The temperature coefficient of the parameters with the irradiated material suggests possible changes in electron transfer energies and a decrease in the probability of molecular reaction due to gross structural alterations such as vacancy formation brought about by irradiation.

APPENDIX 1

The relation between the decay constant and the interface velocity.

The decomposition proceeds by the advance into the crystal of an interface. One may introduce arguments to show that the parameter k is proportional to the velocity of penetration of this interface. One such argument is as follows: Suppose the decomposing particles are spheres of radius r' and particle size distribution $n(r')$ where

$$n(r') = Ae^{-ar'}.$$

For a real batch of crystals, $n(r') \longrightarrow 0$ as $r' \longrightarrow 0$, but over almost the whole range of r' the above equation will be a good enough approximation. Thus in the real case, $n(r')$ will be zero at $r' = \text{zero}$, will then rise very sharply over a small range of r' and will then fall exponentially. For the colloidal material used in this study, this is not unreasonable. Assume that at $t = 0$ all particles have intact interfaces which, as decomposition proceeds, ^{penetrate} the crystals at a velocity v cms/s. Then at any subsequent time t , the particle size distribution is represented by

$$n(r,t) = Ae^{-a(r + vt)}$$

which is equivalent to saying that particles of size vt at $t = 0$ will stop contributing to the reaction at time t . A particle of radius r contributes to $\frac{da}{dt}$ an amount proportional to its surface area, i.e. proportional to r^2 . Hence,

$$\begin{aligned}
\frac{da}{dt} &= c \int_0^{\infty} r^2 n(r,t) dr \\
&= c' \int_0^{\infty} r^2 e^{-a(r+vt)} dr \\
&= c' e^{-avt} \int_0^{\infty} r^2 e^{-ar} dr \\
&= c' (2/a^3) e^{-avt} \\
&= C e^{-avt}
\end{aligned}$$

Therefore $\alpha = \alpha_{\infty} (1 - e^{-avt})$ ($\alpha = 0$ at $t = 0$). This is the same as penetration equation 2 with $k = av$. Hence k is related to the interface/velocity by a constant of the system "a" with dimensions L^{-1} . Thus the slope of the Arrhenius plot for k represents the true activation energy for the velocity of interface penetration and the corresponding frequency factor will be directly related to that for the interface penetration velocity (see Appendix 11). In the above argument, the assumption of cubes or any other solid form instead of spheres does not alter the final outcome mentioned in the previous sentence, since the term e^{-avt} always remains.

Other topochemical models were adopted and all appear to relate the slope of the Arrhenius plot for k with the activation energy for interface penetration. It might be mentioned in passing that the particular particle size distribution mentioned above might well explain the kinetics of decay of a host of reactions observed to be of the first order. Even if a simple particle size distribution, such as crystallites of the same dimensions are used, the process of random cracking which occurs with most

thermal decompositions even down to sub-grain levels probably ensures some exponential form of particle size distribution. Such an argument was put forward in connection with the KBrO_3 decomposition.⁽¹⁷⁾

APPENDIX 11

Relationship between the molecular vibration frequency and the observed pre-exponential factor for k.

The following crude picture relates the observed pre-exponential factor for k with the molecular vibration frequency. Let the molecules vibrate with frequency $\nu_0 \text{ sec}^{-1}$. Assuming reaction occurs at every vibration which possess energy in excess of the activation energy U , then the fraction of any layer of molecules reacting per sec. = $\nu_0 \exp(-E/RT)$. The velocity of penetration of the reaction into the crystal is therefore $v = h\nu_0 \exp(-E/RT)$, where h is the thickness of one molecular layer. Now $k = av = ah\nu_0 \exp(-E/RT)$. Hence the observed pre-exponential factor = $ah\nu_0$ where "ah" is a constant of the system. The decrease of the observed frequency factor with irradiation is $\sim 10^4$. It is, of course, not possible for h to be much effected by irradiation and the only possible effect on "a" would be to increase it (subdivision by cracking) which would imply an even lower ν_0 . It is thus not possible to relate the drop in frequency factor to the topochemical quantities "a" or h but rather to some more fundamental microscopic event such as a fall-off in rate of collision between two azide groups mentioned in the discussion, etc.

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TABLE 1

Values of m over the acceleratory region for different t_0 corrections.

(The maximum rate occurs at $t = 220$ mins)

<u>t_0</u> (mins.)	<u>m</u>
0	6.5
28	5.0
56	4.3
84	3.7
112	2.7
138	2.2

TABLE 11

Uncorrected and corrected values of the power m for various runs.

<u>Uncorrected</u>	<u>Corrected</u>
3.7	2.0
5.2	1.1
6.5	2.2
4.7	2.6
2.7	1.8
6.1	2.0
6.0	2.2
4.3	1.7
5.4	2.0
7.2	2.4
<u> </u>	<u> </u>
Average 5.1	Average 2.0

FIGURE CAPTIONS

Fig. 1 Fraction of total decomposition, α , vs. time.

Full circles; experimental points for unirradiated material at 240.9°C

Open circles; experimental points for irradiated material at 238.5°C

Other points are the attempted fits indicated by arrows

Fig. 2 Logarithmic plot of α vs. time

Fig. 3 Arrhenius plot of $1/\tau$ (unirradiated); full circles and $1/\tau$ (irradiated); open circles. In the lower straight line, no statistical weight is placed on the upper 3 points.

Fig. 4 Arrhenius plot of $\sqrt{\alpha}$

Fig. 5 Arrhenius plot of $k_{\max}$

Fig. 6 Arrhenius plot of k from the decay stage fit

$$\alpha = \alpha_{\infty} \{ 1 - \exp [- k (t - t_0)] \}$$

Fig. 7 $\alpha_{\max}$ (the value of α at the maximum rate) vs. temperature.