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The Explosive Sensitivity of the Metal Azides to Impact

P. G. FOX

Surface Physics, Cavendish Laboratory, Cambridge, England

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The thermal decomposition kinetics of single crystals of α-lead azide have been studied as a function of surface to volume ratio. As in the case of sodium and thallium azides previously reported by Walker, Gane, and Bowden, the decomposition is directly proportional to the surface area of the decomposing crystal and the temperature dependence of the rate is given by

$$\text{Rate of decomposition (molecules m}^{-2}\text{ sec}^{-1}) = 7.4 \times 10^{30} \exp\left[\frac{-(123 \pm 6) \times 10^{3}}{R\cdot T}\right],$$

where the activation energy is in units of kilojoules per mole.

These results together with those of Walker, Gane, and Bowden, allow a direct comparison of the relative rates of decomposition for all three materials. This is found to be Na > Tl > Pb over most of the temperature range studied which is in the reverse order of explosive sensitivity. In rationalizing this observation with the thermochemical hot spot theory of explosion, consideration is given to the alternative tribochemical mechanism of initiation and it is proposed that the release of elastic strain energy when a fast crack runs through the material, if conserved at the crack tip, may be used to initiate the decomposition reaction.

The criterion for the effectiveness of this mechanism is taken to be the ductile-brittle transition temperature. From measurements of the elastic-plastic properties of the three azides, it is found that at low-strain rates (10^{-5} sec^{-1}), these temperatures are not high enough to sustain an explosive reaction. However, evidence is given that on increasing the strain rate to that normally associated with impact, lead azide becomes rapidly more brittle and hence more susceptible to fracture initiation. Finally, some implications of the fracture mechanism are discussed and it is shown that preliminary experimental results are in accord with the predictions which such a mechanism allows.

Introduction

It is unlikely that the thermal decomposition of the metal azides would be of unique interest were it not for the fact that, while all can be made to decompose slowly, some revert to a very rapid mode of decomposition which takes place in about a microsecond and the crystal is seen to explode. This curious property is therefore of some interest not only from the fundamental point of view but also because of the practical problems involved in the preparation and handling of such materials.

Two hypotheses have been proposed to explain this phenomenon. The first and perhaps most widely held view dates back to the middle of the last century and was originally applied to gaseous explosions. According to this, heat is generated chemically within a limited volume at such a rate that the temperature rises very rapidly, the rate of rise being limited by the thermal conductivity of the surrounding medium. In a solid this is envisaged as giving rise to a "hot spot." The theory of such thermochemical explosions has been formalized by Frank-Kamenetskii (*1*) and applied to specific geometries, for examples, by Rideal and Robertson (*2*) and Boddington (*3*). Methods of hot spot formation have been demonstrated in an elegant series of experiments by Bowden and Yoffe and their co-workers (*4*).

The second hypothesis, sometimes called the tribochemical mechanism, is less well-defined and has received much less support due to the difficulty of obtaining conclusive experimental evidence. First proposed by Taylor and Weale (*5*) as a possible explanation of their results on the impact sensitivity of secondary explosives, the tribochemical mechanism envisages that molecules on the surface of a crystal may be mechanically activated by the rubbing or shearing of one crystal against another such as may occur on impact of a polycrystalline mass of material. This idea has been discussed several times by Ubbelohde (*6*). The idea of mechanical activation was revived in somewhat different form by Carl (*7*), who imagined that when a crystal of an exothermic material is broken, the lattice energy could be utilized in initiating the chemical reaction. This is not strictly a tribochemical process.

The main purpose of this paper is to combine the common sense of the former hypothesis with the spirit of the latter in the hope that by so doing, at least some of the discrepancies that make the hot-spot theory unsatisfactory for explaining explosion phenomena in the metal azides, may be resolved. But first, we present the results of a study of the slow thermal decomposition of α-lead azide single crystals because these together with a previous similar study of sodium and thallium azides (*8*), provide the first direct comparison of the relative thermal reactivities of a series of azides which vary enormously in explosive sensitivity. Then we consider the mechanical properties of the three azides in relationship to their thermal and explosive reactivities and, in particular, results are presented for the temperature and stress dependence of the strain rate for crystals stressed in uniaxial tension.

Finally, the problem of the transition from slow decomposition to explosion in solids is examined and a mechanism is proposed which is consistent with the experimental observations that the decomposition reaction is surface controlled and that the explosive reaction in lead azide is sensitive to low energy shocks (e.g. ~ 1 kbar). This mechanism is also consistent with the relative reactivities of the three azides studied.

Experimental

Kinetics of Decomposition of α-Lead Azide

Pressure-time curves were obtained with the apparatus shown in Fig. 1. Measurements were made with the system isolated from the ion pump and by using small enough samples, complete decomposition could be followed in the pressure range 10^{-11}–10^{-7} bars (10^{-8}–10^{-4} Torr). Two types of sample were used: individual single crystals of up to 1 mm in length and clusters of noninteracting single crystals of uniform size in the range 10^{-5}–10^{-7} m. These were prepared by the droplet technique already described (*8*). The range of surface to volume studied was 10^3 m^{-1}.

During decomposition, the evolution of nitrogen was followed by monitoring the increase of the mass 28 peak with a mass spectrometer. The total gas

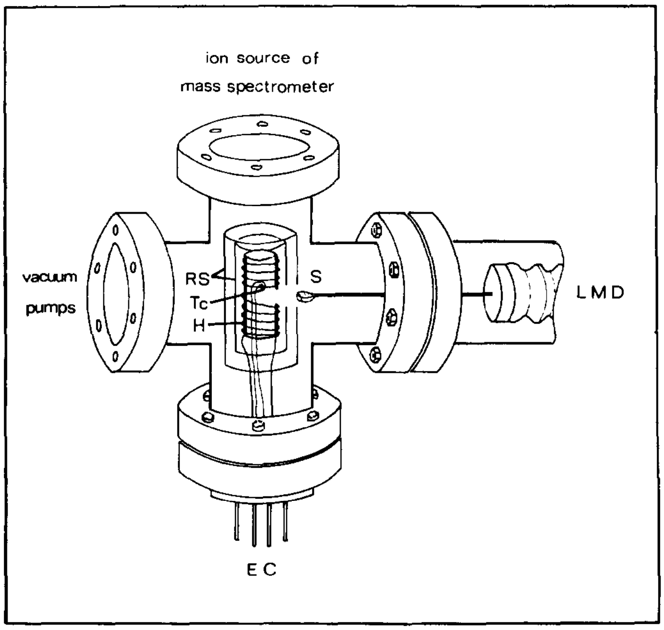

FIG. 1. Apparatus for measuring the decomposition kinetics of single crystals of lead azide. The crystal in the spoon S is inserted into the silica tube furnace H by the linear motion drive LMD Good thermal insulation is ensured by the radiation shields RS. The temperature is measured with the Pt/Pt-Rh thermocouple Tc. Electrical connections are made at EC.

phase composition was checked periodically for the presence of impurities. For those experiments in which the reaction was fast enough to be completed in a time of about a minute or less, the mass spectrum was displayed on an oscilloscope screen and recorded photographically.

Gauge pumping was eliminated by operating the total pressure gauge at 40 μA filament emission. There was no noticeable pumping in the ion source of the mass spectrometer.

Tensile Property Measurements

Crystals of lead and thallium azides are not normally available in lengths greater than about 1 mm and so rather sensitive techniques were necessary for measuring the elastic and plastic properties of these materials. These measurements were achieved with the microtensile testing machine devised by Marsh (*9*) and experiments at room temperature were made following the technique described by him. Experiments above room temperature were possible by surrounding the specimens and grips of the machine with a small tube heater. For these high-temperature measurements, the silica grips were replaced with tungsten rods and 'Araldite' epoxy resin was used to attach the crystal to the rods. After suitable curing the creep properties of the glue and grip assembly were acceptable. Specimens of sodium azide were cleaved from larger crystals grown from aqeuous solution in a manner similar to that described for those crystals with which kinetic data were obtained (*10*). Because sodium azide is rather hygroscopic and the possibility that dissolution of surface layers of the crystal may markedly affect its plastic behaviour, tensile measurements on this material were carried out in a dry atmosphere.

Materials

Lead azide was prepared by adding an excess of 10% hydrazoic acid solution to a solution of AnalaR reagent lead nitrate. The crystals which formed were a mixture of the allotropic forms of lead azide from which crystals of the α form could be selected. The very small crystals of lead azide used in the kinetic experiments were prepared by the droplet method described in Section 1 of the paper by Walker, Gane, and Bowden. Some difficulty was experienced in obtaining these small crystals free from the basic lead carbonate contamination which forms by reaction of the azide with CO_2 in moist air. This was largely overcome by using saturated solutions of lead azide prepared from deaerated doubly distilled water and collecting the crystals in an atmosphere of dry argon.

Fresh samples of lead azide were prepared and used immediately for each experiment carried out. This was an attempt to minimize the uncertain effects of "ageing" (*11*) and to reduce the contamination by basic lead carbonate which, in the case of the very small particles, led to markedly irreproducible decomposition kinetics. By taking these precautions, the average contamination did not amount to more than one monomolecular layer for the very small crystals and about one tenth of a monolayer for the large crystals as judged by the total amount of CO_2 evolved on decomposition.

Thallous azide was prepared by a similar method to that for the lead compound. The sparingly soluble material was precipitated in alkaline solution by the addition of ammonium hydroxide solution. Crystals were obtained by crystallization from hot solution which gave a mixture of imperfect octahedra and needles. Almost all of the latter were hollow along their axes and great care was necessary in selecting specimens which were suitable for the tensile tests.

Sodium azide crystals were grown by slow evaporation of the aqueous solution formed by adding a slight excess of 10% hydrazoic acid to a solution of AnalaR sodium hydroxide.

Results

Decomposition Kinetics

Typical data for the kinetics of decomposition of both individual single crystals and clusters of single crystals are shown in Fig. 2 and are derived from continuous traces of nitrogen evolution plotted as a function of time. The two outstanding features of these plots are (i) the existence of linear portions which extend in some cases to over 50% decomposition, and (ii) the decomposition starts without a significant induction period.

Linear rates of decomposition are usually associated with reaction at discrete sites at the surface. These may be product nuclei or surface irregularities such as steps, cracks, or linear imperfections, e.g., dislocations (*12*). However, despite many publications invoking dislocation models to explain reactivity in solids, the evidence relating defect structure to kinetics by anything more than conjecture, is extremely sparse (*13*). This is indeed the case for lead azide in which scanning electron microscopic examination of partially decomposed crystals has failed to reveal decomposition nuclei at magnifications up to 30,000. Also, a detailed study of replicas taken at the earliest stages of decom-

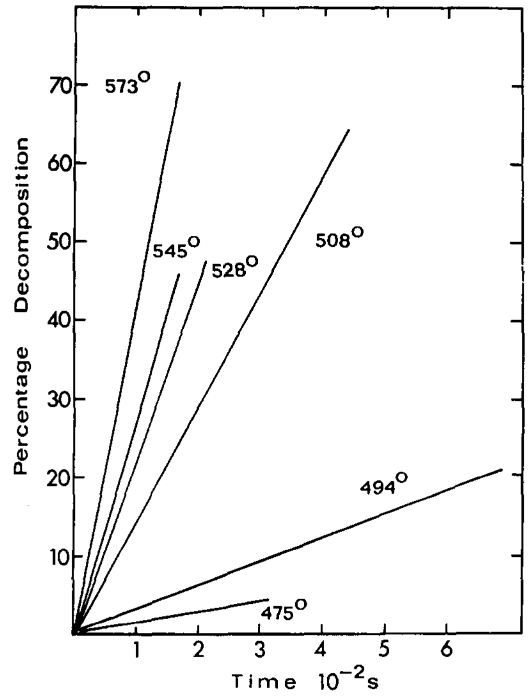

FIG. 2. Pressure-time curves for the decomposition of lead azide showing the extent of the linear portions of the curves. Percentage decomposition is based on measured nitrogen pressures. Temperatures in °K.

position, shows that lead is formed uniformly over the entire surface and not preferentially at surface features although these exist on most crystals.

The role of dissolved or occluded impurities in creating sites at which decomposition can occur, may be important. Reitzner has suggested that the length of the induction period in the initial decomposition of the metal azides is related to the evolution of impurities, such as water, from the crystal. This is assumed to react chemically with germ nuclei which catalyse the reaction, and until this impurity reaction is complete, the decomposition does not accelerate (*14*). Evidence that the length of the induction period is related to impurity content of the crystal has recently been presented for the series of azides discussed here (*15*). These impurities are especially prominent in the gas phase during the decomposition of sodium azide and may be responsible for producing the sites at which the relatively small amount of decomposition which is normally associated with this material, occurs (*16*). Impurity effects are less prominent in the decomposition of thallium azide and are apparently nonexistent in the decomposition of lead axide which also, in these experiments, shows no induction periods even at the lowest temperatures studied (400°K). Moreover, a detailed mass spectrometric examination of the gas phase during the early stages of decomposition showed that only minute amounts of water were present and no peak corresponding to hydrazoic acid could be detected.

Figure 3 summarises all the rate data as a function of temperature and surface area for both types of specimen. The graph shows clearly the dependence of decomposition rate on the surface area over a wide range of temperature and also the good reproducibility of the results. The equation for the line of best fit to the data is

Rate of decomposition (molecules m^{-2} sec^{-1}) =

$$7.4 \times 10^{30} \exp\left[\frac{-(123.2 \pm 6.3) \times 10^{3}}{R \cdot T}\right],$$

where R is in units of $Jmole^{-1}$ deg^{-1}.

In Fig. 4 the data for all three azides are compared. That for sodium and thallium azides is derived from the results of Walker (*17*). From this we see that, over most of the temperature range, lead azide is the least reactive and that above about 620°K, sodium

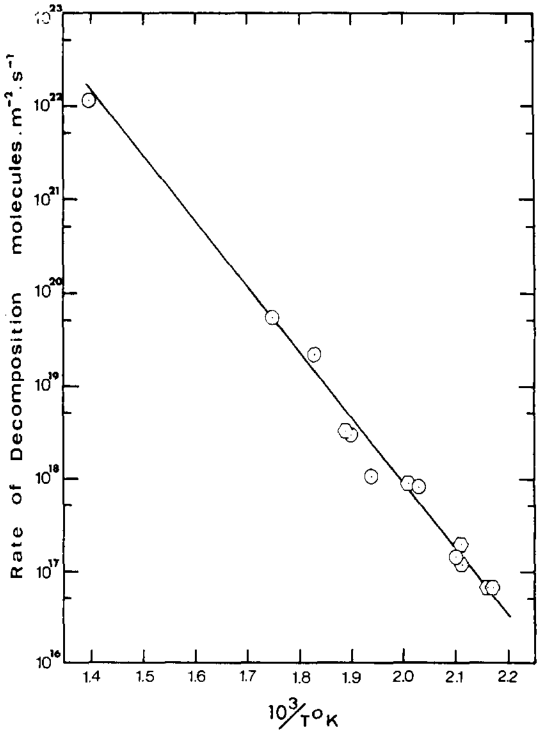

FIG. 3. Arrhenius plot for the thermal decomposition of lead azide. o represents data for individual single crystals and ○ are for clusters of small uniformly sized crystals. The rates are calculated from the linear portions of the curves.

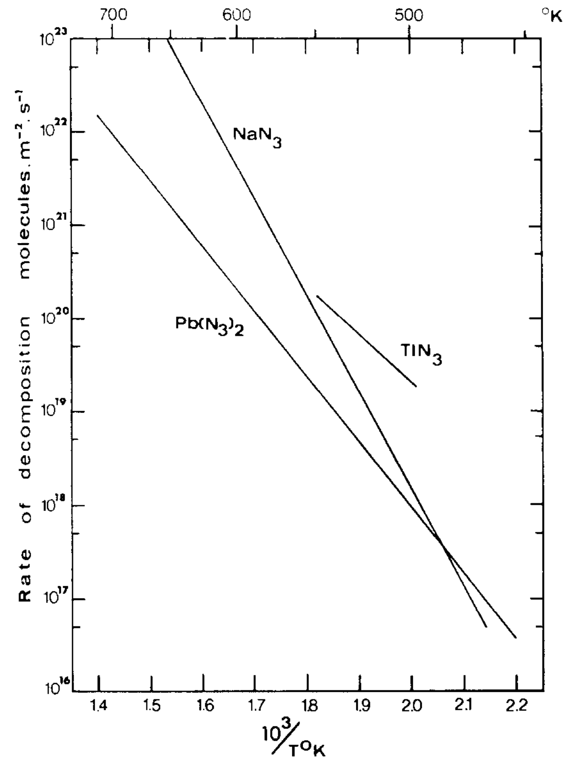

FIG. 4. Direct comparison of the rates of thermal decomposition of lead, thallium, and sodium azides in the temperature range studied for each material. The results show that over most of the temperature range lead azide is the least reactive.

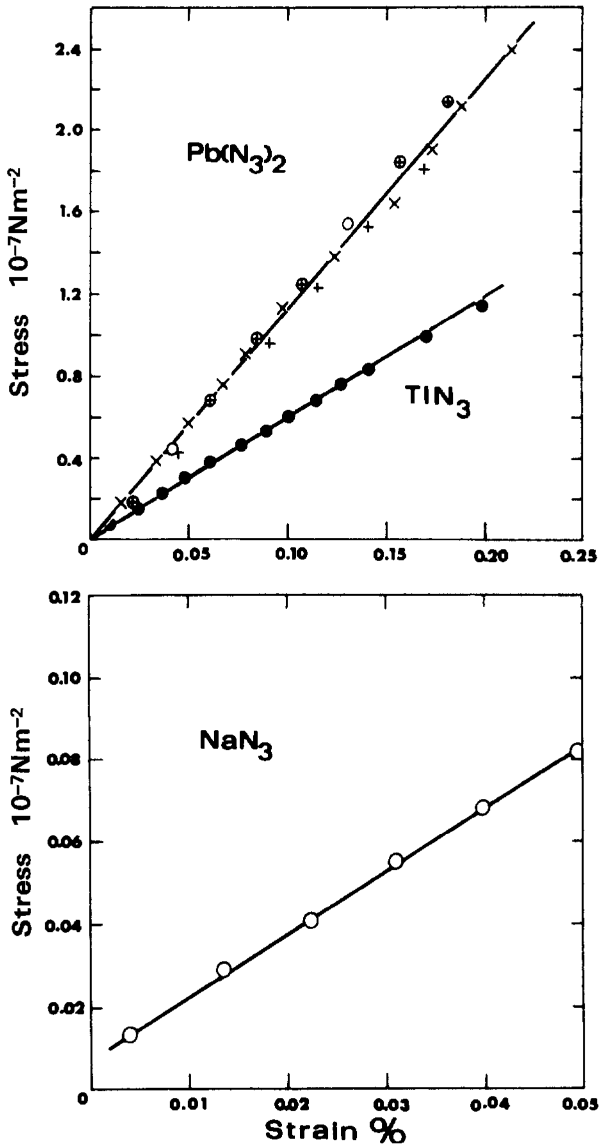

FIG. 5. Stress–strain data for lead, thallium, and sodium azides. The different symbols for lead azide illustrate the reproducibility of the data during successive loadings.

azide reacts more rapidly than either lead or thallium azides. These observations are in contrast to the observed order of explosive sensitivity, the exothermicities of the compounds and predictions of reactivity based upon band structure considerations (*18*), and imply that the explosive reaction is not simply related to the balance of thermal energy as predicted by the hot spot theory and also that the size of the band gap is not the prime factor in determining the rates of slow thermal decomposition in these materials.

Tensile Measurements

All three azides behave elastically under short-term loading. Moreover this behaviour is reproducible for tests carried out consecutively, Fig. 5. Their strengths are such that breaking stresses of about E/100 are common. The Young's moduli determined were as follows: lead azide, $E_{[100]} = 1.62 \pm 0.52 \times 10^{10}$ Nm^{-2} (15); thallium azide, $E_{[001]} = 0.62 \pm 0.01 \times 10^{10}$ Nm^{-2} (6); sodium azide, $E_{[1000]} = 0.17 \pm 0.07 \times 10^{10}$ Nm^{-2} (13). The subscripts refer to the direction of the tension axis and the figures in parentheses represent the number of tests in each case. (1 Newton (N) = 10^5 dynes.)

In comparison with metals and some other non-metallic compounds, these azides are brittle materials sustaining strains of only a few tenths of a per cent before fracture. However, at constant stress, all show measurable creep and some typical results are shown in Fig. 6. The reproducibility of the creep data from one specimen to another is generally

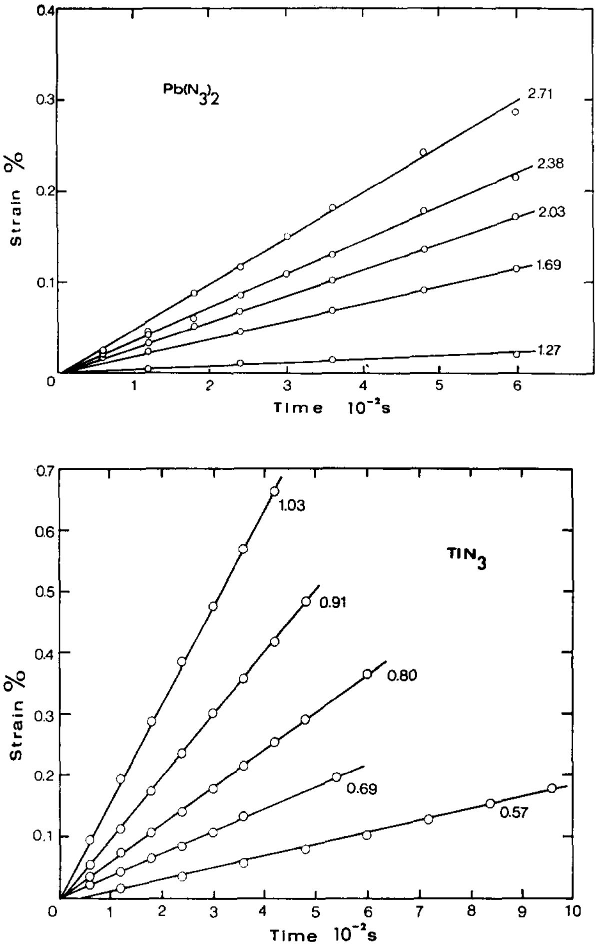

FIG. 6. Strain rate data for lead and thallium azides at 293°K. The stress is shown for each curve in units of 10^{-7} Nm^{-2}.

rather poor especially for sodium azide in which "negative" creep rates (i.e., the specimen contracts under a tensile load) have been measured even at the highest stresses used in these experiments. The reason for this is at present unknown although it may be connected with the phase change which occurs in sodium azide near room temperature (*19*, *20*). It does not appear to be instrumental. A comparison of the strain rates at different stresses for lead and thallium azides is shown in Fig. 7. The strain rate is only weakly dependent upon stress for freshly prepared lead azide and this is also true within limits of experimental error for sodium azide. The temperature dependence of the strain rate is shown in Fig. 8 for lead and thallium azides. The upper temperature is limited to about 426°K due to the thermal instability of the azides and the resultant possibility of decomposition bringing about a change in structure and hence mechanical properties.

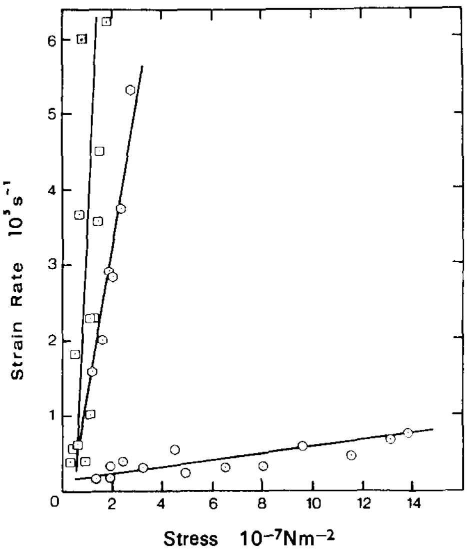

FIG. 7. The stress dependence of the strain rate for lead and thallium azides at 293°K. Because of the large scatter of data, that for sodium azide is not shown. ⊙ Fresh lead azide, ⨀ aged lead azide, □ thallium azide.

Discussion

The main purpose of this discussion is to relate the decomposition characteristics of the azides to the two hypotheses for their explosive sensitivities. Features which have to be incorporated in a consistent theory of sensitivity to mechanical impact, are as follows:

(1) The initial rate of the slow decomposition reaction is surface area dependent.

(2) The relative rates of slow decomposition are in the reverse order of explosive sensitivity to impact.

(3) Lead azide is sensitive to shocks of such low intensity that adiabatic heating in the compressive part of the stress wave is insufficient to initiate the explosive reaction.

The relationship Between the Slow and the Fast Reactions and the Transition to Explosion

In this section we attempt to systematize the observations just described with an hypothesis which is closest to the idea proposed by Carl (*7*). Thus, a mechanism whereby the reaction may propagate rapidly as a surface process, is that involving brittle fracture of the crystal in which some of the elastic strain energy released at the crack tip can be utilized

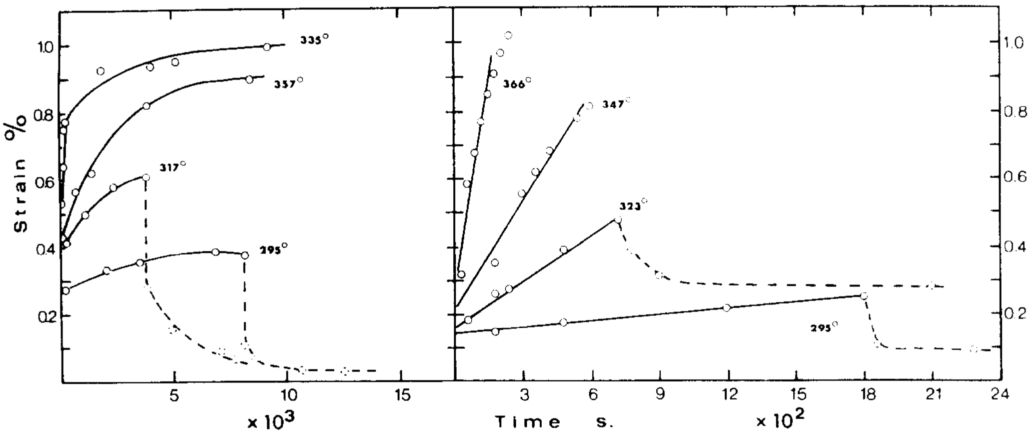

FIG. 8. The variation of strain rate with temperature for lead and thallium azides. Stresses: 2.1×10^7 nm^{-2} for lead azide, 8.0×10^6 Nm^{-2} for thallium azide. The dotted lines show how the strain relaxes when the crystal is unloaded. Temperature °K.

in chemical-bond breaking thereby initiating the chemical reaction. A preliminary description of this process and some results for a group of exothermic and endothermic materials has already been given (*21*). The feasibility of the mechanism depends upon the way strain energy in the lattice is redistributed among the various energy-dissipative mechanisms during crack propagation. In practice some of this must be used in supplying the energy of the new surfaces formed and for energetic (maximum velocity) fractures, some will be dissipated as kinetic energy of the fragments produced. Other dissipative processes such as plastic flow by dislocation movements will decrease the amount of energy available for chemical reaction and fracture, as a method of initiation, will be less effective. In general, this last process will be the most important method of dissipating strain energy. (Plastic energy appears as heat, but since the volume involved in plastic flow is generally large, the temperature rise is small and not itself sufficient to initiate explosion.)

It can be seen that this mechanism is consistent with a surface decomposition reaction and also with the observation that lead azide, e.g., is sensitive to mechanical shocks which are of the same order as the fracture stress of the material. This is essentially a mechanism of initiation for we assume that once the reaction is started, the release of thermal energy from such highly exothermic molecules as lead and thallium azides would be sufficient to sustain the decomposition. (It is interesting to note here that calculations of the rate of evolution of heat during decomposition by using the expression $q \cdot A \exp(-E/R \cdot T)$ where q is the exothermicity of the decomposition reaction, show that this rate becomes the same in lead and sodium azides at 590°K for values of q equal to 484 and 21 kJ mole^{-1}, respectively. This implies that the large exothermicity of lead azide although important in the propagation of the explosive reaction may not be the prime factor in initiation.)

If we now assume that the available strain energy released on fracture is converted into heat as is suggested by the experiments on the thermal decomposition produced by fracture in brittle crystalline solids (*21*), then the present proposal is consistent with the thermochemical ideas of explosive sensitivity in which a hot spot of molecular dimensions travels through the crystal at the fracture velocity.

To test this fracture criterion of initiation, it is necessary to compare the elastic-plastic properties of the three materials whose reactivities have been compared here. For the mechanism to be effective, requires that the minimum amount of energy be lost by plastic flow. This means that the temperature at which the transition from brittle to ductile behaviour should be high enough so that reaction once initiated can become self-sustaining.

A quantitative approach to the ductile-brittle transition temperature starts with the Griffith criterion of crack propagation (*22*) which was modified by Mott (*23*) to give for the velocity of a crack, the expression

$$v_c = A \cdot v_0 \left[1 - \frac{E_s}{E_{el}}\right]^{\frac{1}{2}}.$$

This predicts two important features of the fracture process, namely, that there can be no crack propagation if the elastic energy released E_{el} is smaller than the surface energy E_s required to form the new surfaces and also that the fracture velocity v_c has a maximum value which is some fraction of the velocity of sound v_0 in the material. The value of the numerical factor A is about 0.3 for a wide variety of materials (*24*, *25*). For a fracture process in which some of the elastic energy can be dissipated in plastic flow at the crack tip, the equation above is modified as follows:

$$v_c = A\cdot v_0\left[1-\frac{E_{\mathrm{pl}}}{E_{\mathrm{el}}}\right]^{\frac{1}{2}},$$

which assumes that $E_{\mathrm{pl}} \gg E_s$.

The work done in plastic deformation may be estimated by writing

$$dE_{\mathrm{pl}} = \sigma\cdot d\epsilon,$$

in which $d\epsilon$ can be related to the activation energy Q for plastic deformation by the relationship

$$d\epsilon = B\cdot\sigma\exp\left[\frac{-Q}{kT}\right]dt,$$

whence

$$dE_{\mathrm{pl}} = \mathrm{B}\cdot\sigma^2\exp\left[\frac{-Q}{kT}\right]dt. \qquad (1)$$

For the purpose of this calculation we express the shear stress along a slip plane inclined at an angle θ to the plane of the crack by the simple form (*26*, *23*):

$$\sigma = \mathrm{E}\sin\theta\cdot\left(\frac{a}{r}\right)^{1/2}, \qquad (2)$$

where E is Young's modulus, a is the lattice parameter at the crack tip, and r is the distance in the direction θ from the tip of the crack, of the point at which slip is occurring. This expression for the shear stress is valid provided that $r \gg a$ and because of the rather weak dependence of the ductile-brittle transition temperature on the precise form of the expression for the shear stress, it is doubtful whether more exact expressions (*27*, *28*) which differ only by a numerical factor, are justified in this case for which no precise information on the nature of the slip planes in the three azides is available. (It is understood that although θ may not coincide with the direction of maximum shear stress at the crack tip (*29*), the shear stress resolved along θ will be large enough to produce slip.) The expression given here is derived for a static crack but Broberg (*30*) has shown that as the crack reaches its maximum velocity, the value of the shear stress is reduced to about 0.6 of its static value.

Substituting Eq. (2) in Eq. (1) and integrating leads to

$$dE_{\mathrm{pl}} = B\cdot\mathrm{E}^2\cdot\sin^2\theta\cdot a\exp\left[\frac{-Q}{kT}\right]\int_a^l\frac{dr}{r}\int_0^{l/v_c}dt$$

$$= \frac{B\cdot\mathrm{E}^2}{v_c}\cdot\sin^2\theta\cdot a\cdot l\exp\left[\frac{-Q}{kT}\right]\ln\left(\frac{l}{a}\right).$$

where l is the extent of the plastic zone normal to the fracture surface. Thus equating the elastic and plastic energy terms and substituting

$$v_c = 0.3v_0 = 0.3(\mathrm{E}/\rho)^{1/2},$$

where ρ is the density of the material, allows an estimate of the highest temperature T_{DB} at which a crack will propagate at its maximum velocity (Rayleigh velocity) in the crystal.

$$E_{\mathrm{pl}} = E_{\mathrm{el}}$$

and

$$\frac{B'\cdot\mathrm{E}^2\cdot a\cdot l\cdot\sin^2\theta\cdot\exp\left[\frac{-Q}{kT_{\mathrm{DB}}}\right]\ln\left(\frac{l}{a}\right)}{(E/\rho)^{1/2}} = \frac{\pi\sigma^2\cdot c^2}{4\mathrm{E}}.$$

Because of the strong dependence of crack velocity on temperature, more and more of the elastic strain energy will be dissipated in plastic processes such as dislocation movements as the temperature is increased and the crack will slow down due to blunting at the tip.

The values of B' and Q are known from measurements of the temperature dependence of the strain rate (Fig. 9). E has been measured for each material and values of σ are those for the average breaking stress determined experimentally. The values of l, a, and c to be used in the calculation are less definite. For a we have used the lattice spacing in the direction of crack propagation. The choice of l is based on the observations of Schmidt (*29*) who found that the extent of the dislocated region on either side of a

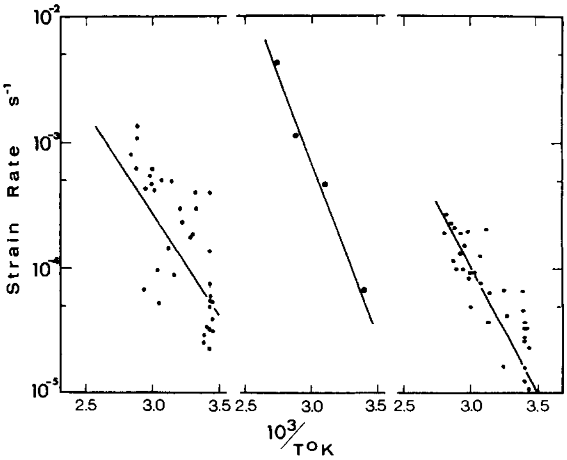

FIG. 9. The temperature dependence of the strain rate for lead, thallium and sodium azides. Information derived from these results is used in the calculation of the ductile-brittle transition temperature T_{DB}.

maximum velocity crack in sodium chloride crystals is ca. 1 μm and we have used this value in all three materials here. The value to be used for c the length of the semielliptic Griffith crack is a matter of considerable conjecture, however estimates for these calculations are based on values for E, σ and an order of magnitude value (10^{-1} Jm^{-2}) of the surface energy. Substitution in the Griffith equation $c = 2\mathrm{E}\cdot\gamma/\pi\sigma^2$ then allows an estimate of c (γ is the surface energy of the fracture plane.)

Two additional points should be mentioned here. The first is that the elastic constants used in the calculations are those parallel to the easiest test directions in the crystals, e.g., parallel to the long axis of the needle in crystals of lead and thallium azides. The required elastic constants are those for directions normal to the planes of easiest decomposition. These two directions may not coincide. For instance, scanning electron microscope observations of the decomposition process, show that decomposition takes place most readily on planes parallel to the linear azide ion. Figure 10 illustrates the relationship between the crystallographic unit cell and the morphology of the "as grown" crystals. Also shown are the directions of decomposition and tension. The azide ions are not shown to simplify the drawings but are situated as follows. In sodium azide the N_3^- ion lies along the diagonal of the unit cell (parallel to the c axis of the hexagonal structure shown) and between two adjacent layers of sodium ions. In thallium azide both ions lie in alternate {001} planes and the azide ions lie along ⟨110⟩ directions. The situation in lead azide is considerably more complex (*31*) in which azide ions of four different symmetries occur, decomposition being fastest parallel to the most labile of the four types of ion, i.e. parallel to ⟨100⟩. In these experiments the tension axis is parallel to the direction of decomposition in lead azide rather than normal to it. However, we assume that because lead azide shows no marked structural asymmetry (this can be readily seen from a model of the structure) little error is introduced in the present calculations by using the value of E quoted here.

The second point is that we shall assume that the mechanical property measurements, which are all carried out in tension, can be applied to the impact problem for which values in compression are more appropriate.

Values for the ductile-brittle transition temperature are listed together with strain rate parameters in Table I.

The two features of this compilation which are of immediate interest are the relative absolute values of the ductile-brittle transition temperatures and the sequence of temperatures Pb > Na = Tl.

The Transition Temperatures

The values of the temperature are all low and certainly below the level where the reaction could become self-sustaining even if it were initiated by the release of elastic strain energy at the tip of a moving crack. However, these values of the transition temperature are for measurements made at low

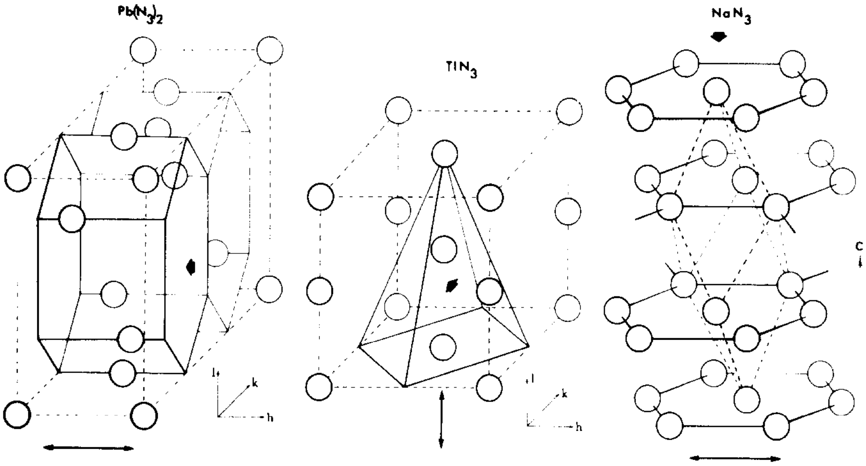

FIG. 10. Geometrical relationships in the three azides. The dotted lines outline the crystallographic unit cells and the full lines represent the morphology of the "as grown" crystals. For simplicity, only the metal ions are shown and these are not to scale. The heavy arrows represent the direction of decomposition which in each case is parallel to the long axis of the azide ion. The light arrows represent the direction of the applied stress during tensile testing.

TABLE I

SUMMARY OF ELASTIC-PLASTIC DATA FOR LEAD, THALLIUM AND SODIUM AZIDES

Material	Young's modulus $Nm^{-2} \times 10^{10}$	Activation energy for creep kJ $mole^{-1}$	Preexponential factor B sec^{-1}	Ductile-brittle transition temp °K	Hardness V.H.N.
$Pb(N_3)_2$	1.62 ± 0.52	30.0 ± 4.8	0.14	405	130
TlN_3	0.62 ± 0.01	52.6 ± 4.4	1.29×10^3	332	46
NaN_3	0.17 ± 0.07	39.3 ± 5.4	1.55	332	10

strain rates, i.e., ca. 10^{-5} sec^{-1} and observations on other ionic solids show that unlike metals, the ductile-brittle transition is extremely sensitive to strain rate. For example Johnston et al. (*32*) have shown that the ductile-brittle transition temperature in magnesium oxide is raised from room temperature to about 2300°K for an increase in strain rate from 10^{-5} sec^{-1} to 40 sec^{-1}. The explosive reaction in lead azide is initiated by impact, i.e., at strain rates in the range 10–100 sec^{-1} and by analogy with the above example, one would expect the transition temperature to increase accordingly. It is not possible to say with any certainty how large this increase will be nor indeed what will be the relative increases for the three azides since these factors will depend upon the type of slip systems operating in each crystal at a particular temperature and also on the effect of impurities on dislocation mobility.

However, from creep data such as that presented in Fig. 8, we see that lead azide shows a marked tendency to work harden more rapidly than thallium azide which suggests that the transition temperature in $Pb(N_3)_2$ may increase more rapidly with strain rate than that in TlN_3. This is also reflected in the larger preexponential factor for TlN_3 shown in the Table I in which the value for NaN_3 is intermediate.

Some further evidence for the effect of strain rate is provided by the results of hardness measurements on $Pb(N_3)_2$ and NaN_3. The indentation hardness of a crystalline material is a measure of its resistance to plastic deformation, i.e., the difficulty of operating dislocation sources around the indentation. Moreover under the conditions of the test and at nominally low loading speeds, the deformation rate corresponds to strain rates which, for the results given here, are in the range 10^{-2}–10^{-3} sec^{-1}. Table I shows that NaN_3 is markedly more ductile than $Pb(N_3)_2$ whereas at the low strain rates of the experiments already described, the two materials are not widely different (Fig. 9). Additionally by using the approximation that the yield stress is one third of the hardness (*33*) we see that the yield stress in $Pb(N_3)_2$ increases from about 10^7 Nm^{-2} at low strain rates to about 5×10^8 Nm^{-2} at the higher strain rate whereas the corresponding figures for NaN_3 are 0.5×10^7 Nm^{-2} to 3×10^7 Nm^{-2}.

Reasoning along these lines suggests, therefore that under impact lead azide is likely to behave in a more brittle manner than NaN_3 thus providing the right conditions for fracture initiation of the explosive reaction. The values of the transition temperature also suggest that the fracture mechanism would predict an order of increasing ease of initiation of $Pb > Na = Tl$. This is conditional on how the transition temperature for each material varies with strain rate up to that corresponding to impact. The results already published on the amount of chemical reaction produced by fracture in lead and sodium azides show that under these conditions the former is somewhat more reactive than the latter (*21*) implying that initiation by this mechanism is easier in lead azide than in sodium azide. Whether the reaction develops explosively will depend upon its subsequent chemistry and propagation is undoubtedly dependent in lead azide on the fact that it is considerably more exothermic than sodium azide.

At this point it is interesting to consider an important consequence of this line of reasoning. It has been suggested that one method of initiating an explosive reaction in materials like the azides is by the generation of local hot spots by frictional heating (*34*). Indeed, Bowden and Ridler had already shown that very large local temperatures can be generated by rubbing together two dissimilar metals (*35*). However, we know from the work of Taylor and Qinney that frictional heating in metals is produced by the very efficient degradation of the work of plastic deformation to heat (*36*). Since in the present situation we are dealing with very brittle materials in which plastic deformation is extremely small at high strain rates, frictional hot spots would seem an unlikely mechanism for initiation.

The Evidence for the Fracture Initiation of Explosive Reactions

An attractive feature of the fracture mechanism of initiation is that some predictions can be made about the course of the explosive reaction which make it possible to test the hypothesis. For instance, fracture velocities are limited by the elastic properties of the material and this sets an upper limit on the speed at which the explosive reaction can travel. Moreover, it should be possible to show that the energy release rate at the crack tip is high enough to enable the reaction to become self-sustaining. Tests of both of these predictions have been made experimentally.

Young's modulus gives a value of about 1 km sec^{-1} for the fracture velocity in lead azide. In order to attain this linear rate of decomposition, the kinetic results show, by extrapolation, that the temperature needs to be raised to about 900°K. Recent measurements of the explosion velocity of single crystals of α-lead azide by M. M. Chaudhri in this laboratory show that for unconfined crystals this velocity is indeed in the region 1100–1300 $msec^{-1}$. Similarly from independent measurements of the amount of decomposition produced by brittle fracture in lead azide (*21*), we infer that the temperature generated at the tip of the crack is very large. From these results we see, therefore, that a mechanism of initiation based on fracture is possible.

Conclusions and Consequences

We have examined a mechanism whereby initiation of the explosive reaction in the metal azides is dependent upon the mechanical properties of the crystal. This mechanism would operate under the impact conditions commonly used in practice. Inherent in the discussion is the assumption that the chemical reaction itself plays a minor role at this stage and only subsequently becomes important as the reaction develops into an explosion.

The fracture mechanism has the advantages of predicting the correct velocity for the explosive reaction, is consistent with the observation that reaction takes place at the surface of the crystal and can explain why, for example, lead azide is sensitive to shocks of the order 10^8 Nm^{-2} (1 kbar) which is about the fracture stress of lead azide.

However, the explanations given here contain certain implications which are as follows:

(i) The velocity of explosion is limited for unconfined single crystals to the Rayleigh velocity in the solid. This seems to be confirmed experimentally for lead azide. In addition the *maximum* velocity of explosion cannot exceed the longitudinal stress-wave velocity in the crystal and this will occur when the stress waves are efficiently reflected from the interface between the crystal and its surrounding medium. (An observation of Rogers quoted by Bowden and Yoffe (*4*) that the explosion velocity in silver azide is 4.4 km·sec^{-1} does not seem to have been substantiated by the direct high speed camera measurements of Chaudhri who has found the maximum velocity to be near that of the longitudinal stress wave velocity in the material).

(ii) The fracture mechanism implies that explosion takes place in the solid rather than the liquid or gaseous state.

Evidence that very fast reactions do in fact take place in solids seems to be somewhat sparse in the literature. The group of explosives which are classified as secondaries or high explosives consists of a series of low-melting organic compounds and it is possible that fast reaction in these materials is preceded by melting and vaporization under which conditions detonation velocities of several kilometres per second can be explained on the basis of the thermo-hydrodynamic theory (*37*, *38*). At the other extreme is lead azide which is a solid up to at least 820°K and explodes as the solid. Intermediate in behaviour is silver azide which has a low melting point (524°K) and may explode, under impact, in the liquid state.

Finally, mention may be made of the "waywardness" of lead azide in its explosive behaviour. One of the greatest hazards in the manufacture and handling of this material stems from its unpredictable behaviour towards external stimuli. For instance, while explosion can occur apparently spontaneously, an explosion reaction can also partially propagate in a crystal and then suddenly stop, leaving behind unreacted material. It seems that the essentially localized nature of the fracture method of initiation is better able to explain such behaviour than an explanation based on the bulk hot spot idea.

Perspective

It is appropriate at this stage to try to assess the importance of the fracture mechanism in the explosive behaviour of the azides in a practical situation.

Practical applications of lead azide as a detonator of high explosive reactions, involve the use of the material in finely divided form. The possibility of starting the explosive reaction by adiabatic heating of the gas pockets trapped between the crystals of an agglomerate is therefore very strong (*39*). Chaudhri (*40*), using the high speed camera, has demonstrated recently the ease of initiating single crystals of lead and silver azides by rapidly collapsing bubbles of gas on to the crystal using low-intensity shock waves and it seems reasonable to suppose that this is the most likely mechanism for starting the explosive reaction in compacts of such crystals. We believe, however, the the fracture mechanism of initiation may be responsible in some cases for the sudden and often unexplained explosions which occur in handling lead azide and which makes this material so hazardous to use.

The observations of Cachia and Whitbread (*41*) that removal of the intercrystalline gas in an explosive compact does not change its sensitivity appreciably, may be rationalized on the basis of the fracture mechanism, by bearing in mind that fracture itself is capable of producing gaseous decomposition products which in the case of the organic secondary explosive materials consist of highly reactive free radicals (*21*).

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