

Fast Reactions in Solids

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VIII

SPONTANEOUS EXPLOSIONS

A NUMBER of solids and liquids are known which may explode spontaneously for no apparent reason. Such explosions have been observed during the growth of lead and mercuric azide crystals from suitable solutions under a variety of conditions; chlorine azide (ClN_3), bromine azide (BrN_3), iodine azide (IN_3), nitrogen chloride (NCl_3), cupric azide ($\text{Cu}(\text{N}_3)_2$), and silicon azide ($\text{Si}(\text{N}_3)_4$) are very sensitive materials and often explode at room temperature; $\text{Pb}(\text{N}_3)_4$ decomposes in solution and cannot be isolated as a solid. No satisfactory explanation has, as yet, been given for the occurrence of explosions during growth from solution. The main difficulty is the design of suitable experiments to separate the many variables which could contribute to the initiation of the explosion. Some preliminary experiments have been made, however, and this chapter describes some of the results. The relation between structure and stability discussed in Chapter IV does help in our understanding of some of the phenomena¹.

Another type of explosion which is conveniently discussed in this chapter results from the exposure of a fresh surface. Nitrogen iodide is a compound which belongs to this class (see also Chapter VII) and it has been shown that nitrogen iodide can explode at room temperatures when ammonia is removed from the surface of the solid material^{2, 10}.

THE SPONTANEOUS EXPLOSION OF LEAD AZIDE AND MERCURIC AZIDE

Lead azide $\text{Pb}(\text{N}_3)_2$ and *mercuric azide* $\text{Hg}(\text{N}_3)_2$ can exist in two allotropic forms. In the case of lead azide, one crystal modification is (α) orthorhombic and the other (β) is monoclinic^{3, 4}. α -lead azide which is the stable modification is prepared as a white precipitate by rapid mixing of a solution of sodium azide with a solution of lead acetate or lead nitrate; β -lead azide is usually prepared by the slow diffusion method described by Miles³, and it is obtained in the form of needles when aqueous solutions of sodium azide and lead nitrate inter-diffuse slowly. Table XXVIII summarizes the crystallographic relations of α - and β -lead azide^{3, 5, 6} (see paper by Gray and Waddington⁶).

It has often been stated that β -lead azide is much more sensitive to shock than α -lead azide^{3, 4}, and that large crystals of β -lead azide in particular are extremely sensitive. One suggestion that has been put forward is that the high sensitivity of the large crystals is due to the presence of internal strains in the crystal, and for this reason, lead azide is normally prepared in a finely divided form (dextrinated azide). Recent work has, however, cast doubt on both these statements. Thus Gray and Waddington⁶ have shown that there

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is little difference in the enthalpies of formation of α - and β -lead azide; they find that when there is a difference in sensitivity between azides there is usually a considerable difference in the enthalpies of formation (see APPEN-

TABLE XXVIII

Properties of the two crystalline modifications of lead azide PbN_6

Species	Unit cell size and shape, Å			No. of molecules in unit cell	Enthalpy of formation $\Delta^{\circ}H_f$, kcal/ mole ⁻¹	Density
	a	b	c			
Orthorhombic α HPbN ₆	6.628	11.312	16.246	12	115.5	4.71
Monoclinic ($\phi = 90^{\circ} 10'$) $\beta = PbN_6$	5.090	8.844	17.508	8	115.8	4.93

DIX 3). Further, Hawkes and Winkler⁷ have prepared large crystals of β -lead azide, which were stable over long periods. Crystals 3–4 mm long were relatively insensitive and did not explode even when crushed or broken.

EXPLOSION DURING GROWTH OF β -LEAD AZIDE

Miles³ prepared β -lead azide by allowing a solution of sodium azide to diffuse into a solution of lead nitrate (see, for example, Figure 70). The lead azide which is formed separates as a mass of long needle-shaped crystals.

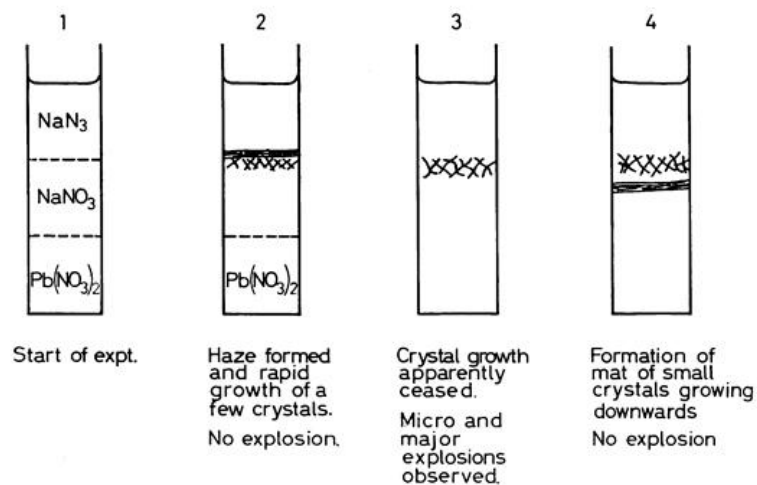


Figure 70. The diffusion growth of β -lead azide

Miles found that spontaneous explosions could occur during the growth period. When isolated, however, the β -crystals, some of which were 4 cm long, were not found to be particularly sensitive. The β -lead azide tends to revert to the α -form, which is the stable modification, under the conditions of

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the diffusion experiments, i.e. by contact with a solution of a lead salt. *Figure 71* shows this transformation taking place in water containing a crystal of α -lead azide at room temperature¹⁴. The transformation also takes place when β -lead azide is kept at a high temperature, ca. 160°C.

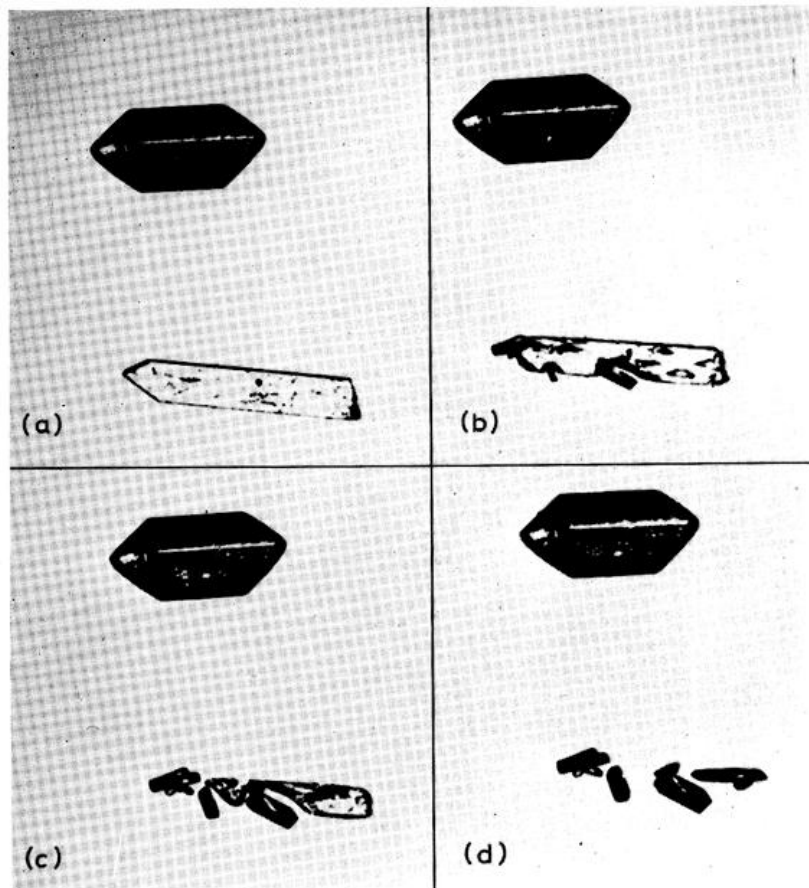


Figure 71. The transformation of β -lead azide into α -lead azide in the presence of a crystal of α -lead azide in solution (after Azäroff¹⁴)

An attempt has been made by Rogers and Harrison⁸ to determine the conditions necessary for explosion during the growth of β -lead azide. In one series of experiments three solutions were carefully introduced into a test-tube so that they did not mix (see *Figure 70*). The bottom layer consisted of 2 c.c. of 20% lead nitrate; the middle layer was 1 c.c. of 20% sodium nitrate; the top layer was 2 c.c. of 10% sodium azide. Crystals of lead azide form somewhere in the sodium nitrate layer after a short time, ca. $\frac{1}{4}$ – $\frac{1}{2}$ hr, and appear to start from the vessel walls and spread inwards. A major explosion of the system generally occurs after the crystals have been growing for 6 to 12 hr. Careful observation has shown, however, that a series of very small explosions can precede the major explosion. During the growth of the crystals audible

'clicks' are detected. These 'clicks' may be tape-recorded or sometimes seen as a tiny flash of light in a darkened room. The solutions do not appear to be disturbed. A major explosion always follows soon after a series of weak explosion 'clicks'.

Spontaneous explosions have been observed under a number of conditions. For example, if a solution is made up by mixing 0.3 c.c. of 5% lead nitrate, 0.3 c.c. of 2% sodium azide, and 2 c.c. of water no immediate precipitate is formed. Crystals appear after about half an hour and spontaneous explosions may then occur in certain cases. A common feature in all the experiments where crystals have exploded has been that the concentration of azide in the solution around the crystal has been initially only slightly above the saturation value. No explosions have been observed when azide is precipitated rapidly using very much stronger solutions. A small rise in temperature of *ca.* 10°C appears to increase the likelihood of explosion very considerably.

Spontaneous explosions of lead azide also take place when crystallization from saturated solutions in ammonium acetate is induced. A detailed study of the crystallization of lead azide from ammonium acetate solutions has been made by Taylor and Thomas¹⁷. By carefully controlling the concentration of the solutions and the temperature and conditions of cooling they are able to predict the time at which spontaneous explosions will occur. For example, with a 1% lead azide solution in 5% ammonium acetate the conditions of crystallization may be so arranged that explosions are obtained after 40–45 min. With 0.6% lead azide the time is 225–255 min, while with 0.5% lead azide it is *ca.* 480 min. In the experiments using 0.5% solutions of lead azide explosions have been observed in 70% of the experiments; in the surviving experiments large well-defined crystals of lead azide were obtained.

Taylor and Thomas have also carried out a critical experiment to show that the spontaneous explosions are not associated with the large crystals of lead azide that are formed. Using a solution containing 0.7% lead azide, they found that a number of large crystals had formed about 30 min before the predicted time of the explosion. These crystals were filtered and the mother liquor kept. At the predicted time the mother liquor portion exploded, while the filtered lead azide crystals remained intact.

Another observation made by Taylor and Thomas is that it is possible to suppress the spontaneous explosions by the addition of small amounts of various additives such as polyvinyl alcohol, dextrin and other hydrophilic polymers. These compounds are known to alter the crystal habit of a wide variety of inorganic and organic materials.

Several suggestions have been put forward to explain the explosions. Rogers and Harrison consider that traces of a particularly sensitive material might be formed⁸. Harvalik¹⁶ has put forward a thermal mechanism where the heat liberated during aggregation of small crystals in the growth process initiates explosion. The experimental evidence is quite clear. Explosion does not take place in the solution. It is associated with the very early stages of crystallization, and this phase requires close study.

It may be associated with the sudden precipitation of small crystals from a solution which locally is highly supersaturated because the nuclei have been removed by previous crystal growth. A very tentative suggestion is that during the first moment of precipitation, before the condensing molecules

EXPLOSION OF NITROGEN IODIDE AT ROOM TEMPERATURE

have had time to rearrange themselves as a stable lattice, they may possess sufficient mobility to allow a fast reaction to occur¹⁸.

SPONTANEOUS EXPLOSIONS OF α -LEAD AZIDE

It seems that spontaneous explosions can also take place during the growth of α -lead azide crystals¹⁵. If a seed crystal of α -lead azide is placed in a supersaturated solution of lead azide in ammonium acetate, an explosion can take place during the early stages of growth. Explosions are not observed when the crystals are large.

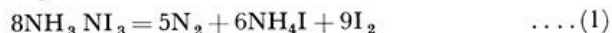
SPONTANEOUS EXPLOSION OF β -MERCURIC AZIDE

When β -mercuric azide is prepared in a diffusion experiment similar to that described for β -lead azide it is also possible to obtain spontaneous explosions. Explosions can be obtained when there are only a small number of β -mercuric azide crystals present. The explosions are much more violent than those obtained with β -lead azide. Mercuric azide also explodes when it is crystallized from hot aqueous solutions.

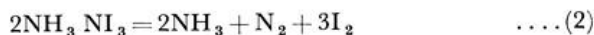
Cadmium azide crystals do not explode spontaneously when grown in a diffusion apparatus. Spontaneous explosions can, however, occur if cadmium azide is prepared by the reaction of cadmium with an aqueous solution of hydrazoic acid. Thomas¹⁷ describes an experiment where a rod of cadmium metal was partly immersed in a 4% solution of hydrazoic acid. A violent explosion occurred after about 30 min. This experiment has been repeated several times with the same result.

THE EXPLOSION OF NITROGEN IODIDE AT ROOM TEMPERATURE

Nitrogen iodide will explode when heated in air at 50°C. The equation representing the decomposition is⁹



Garner and Latchem¹⁰ found that when nitrogen iodide ($\text{NI}_3 \cdot \text{NH}_3$) is dried over a layer of P_2O_5 at a pressure of 2×10^{-3} cm Hg, thermal decomposition could be studied at temperatures below 0°C. However, when the pressure fell below 2×10^{-3} cm Hg, explosion of the nitrogen iodide took place at temperatures as low as -11°C. At low pressures Meldrum^{2, 11} has shown that the equation representing the decomposition is different from that given above,

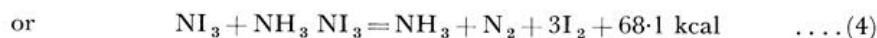
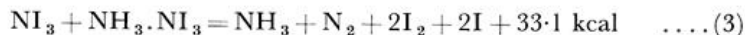


Ammonia and water vapour retard the decomposition of the nitrogen iodide, a pressure of 10^{-3} cm Hg of ammonia being sufficient to stop the reaction.

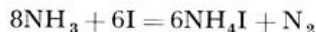
The main effect of gas pressure is to slow down the rate of diffusion of ammonia away from the decomposing surface and so increase the stationary concentration of ammonia at this surface.

The activation energy for Reaction (2) is 18-19 kcal mole⁻¹. It has been assumed that this is the energy required to remove ammonia from the surface of the solid $\text{NH}_3 \cdot \text{NI}_3$. After removal of the ammonia the NI_3 that is left is unstable and decomposes with the liberation of heat. The explosion then grows from this hot region; the reactions proposed being either

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If iodine atoms are produced as in Equation (3) these could react further with ammonia to give ammonium iodide according to the equation (see Equation (1))



It is clear from the results described above that the presence of ammonia can under certain conditions prevent the explosion of nitrogen iodide when the decomposition is brought about by heat (Chapter III), light (Chapter VI), shock (Chapter V), or ionizing radiation (Chapter VII).

The retarding action of ammonia has also been observed in the decomposition of a number of ammonium salts, e.g. ammonium perchlorate (NH_4ClO_4) and ammonium nitrate (NH_4NO_3)¹².

An explosive nitrogen bromide $\text{NBr}_3 \cdot 6\text{NH}_3$ has also been prepared as a dark purple solid¹³. This compound is not stable above -70°C when it explodes to give nitrogen, ammonium bromide, and ammonia.

CONCLUSION

Spontaneous explosions have been observed during the early stages of crystallization of lead azide and mercuric azide. There is no adequate theory to explain this phenomenon. It has been shown that the explosion is not due to a phase change, or to the release of internal strains within the crystal. An experimental investigation particularly of the early stages of crystal growth is necessary.

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