melt is a good solvent both for acidic and basic solutes. On the other hand, the enthalpy of solution of a given solute does not change rapidly with composition. Therefore the enthalpy of solution remains a reproducible quantity despite small variations in melt composition or solute concentration.

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Properties of Lead Azide Prepared in Molten Salt Media

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Crystals are often prepared by precipitation or grown from aqueous solutions. Prepared in this way, often several hundred degrees centigrade below their melting points, they are not in thermodynamic equilibrium and are likely to be more imperfect than crystals grown at higher temperatures. They are traversed by grain boundaries which separate disoriented regions of the crystals having random networks of dislocations and containing isolated and clustered vacancies. The properties of these real crystals can be changed by annealing.[1] Below $0.25T_m$ (T_m = melting point) only defects in special positions near the surface are able to move. Around $0.25T_m$ surface ionic mobility begins to be significant. Above $0.5T_m$ bulk ionic conduction predominates and intergranular adhesion and grain growth become possible. In view of this, attempts were made to prepare inorganic azides at elevated temperatures where some of these defects might be formed in smaller numbers or in less severe form and thus lead to improved stability.

Lead azide is a widely used initiating explosive. Although it explodes before it melts, estimates predict a melting point as high as 500°.[2] Regardless of the accuracy of these estimates, lead azide is made far below its melting point when prepared by the usual procedures of precipitation in aqueous solution. Therefore, it seemed interesting to investigate the preparation of lead azide at elevated temperatures and compare its properties with those of normally prepared samples. Lead azide decomposes at considerably higher temperatures than many other azides. Nevertheless, it is one of the most hazardous azides because of its sensitivity against shock and electrical discharge. Molten alkali nitrates and their eutectic mixtures have solvent properties similar to water.[3] They were found to be suitable media for the preparation of lead, silver, and cupric azides. Also, transition metal azides like cobalt and nickel azides precipitated in molten alkali nitrates. However, cobalt azide is thermally not stable enough and nonaqueous solvents have to be found which would dissolve the alkali nitrates but not the transition metal azides. In preparative quantities only lead and silver azides were made.

Preparation of Lead Azide in Molten Alkali Nitrates as Media

The eutectic mixture of potassium nitrate and lithium nitrate melts at 129°, and that of potassium nitrate and sodium nitrate at 218°. All of these alkali nitrates and their mixtures dissolve alkali azides and many heavy metal nitrates but not heavy metal azides. Therefore, lead azide could be precipitated quantitatively by mixing two separate solutions of potassium azide and lead nitrate in molten alkali nitrates. The precipitation could equally well be performed by dropping finely powdered lead nitrate into a solution of potassium azide in molten alkali nitrates. Both procedures led to lead azide crystals having the same properties. This work was carried out either in beakers on a hot plate or in test tubes which fitted into wells of a temperature-controlled metal block. The melt could be poured into distilled water for separation of the lead azide crystals. However, the melt was usually permitted to solidify and then cool to room temperature. The alkali nitrates were leached out with distilled water and the lead azide crystals obtained by filtration with a sintered-glass filter. The residue was extensively washed with distilled water and finally with alcohol and acetone. The latter wash prevented the lead azide crystals from sticking together, and thus they became easier to handle. Dry lead azide is hazardous and one explosion occurred. Grounding of equipment and using a conductive floor and conductive shoes minimize the danger. Lead azide crystals submerged in molten alkali nitrates or water never exploded during more than 60 preparations.

The lead azide crystals prepared in alkali nitrate melts had a needlelike shape and were obtained in batches of fairly homogeneous crystal sizes. Some batches had an average crystal size of less than 5 μ; other batches, an average crystal size as large as 150 μ. Only analyzed chemicals were used in the preparation and the only impurity which had to be controlled was water. Lead azide was obtained which had a purity of close to 100% when the chemicals used were carefully dried in the solid state and further dehydrated by bubbling dry nitrogen through the melts. Without the drying procedures 99.6% pure lead azide was obtained in KNO_3–$NaNO_3$ melts and 98.0–99.0% pure lead azide

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(1) F. C. Tompkins and D. A. Young, *Discussions Faraday Soc.*, **23**, 202 (1957).

(2) F. P. Bowden and A. D. Yoffe, "Initiation and Growth of Explosion in Liquids and Solids," Cambridge University Press, London, 1952.

(3) B. R. Sundheim, "Fused Salts" McGraw-Hill Book Co., Inc., New York, N. Y., 1964.

in KNO_3–$LiNO_3$ melts. The difference in purity found with these two molten salt systems is understandable since lithium nitrate is hygroscopic and retains more water than the other nitrates. Water in the molten alkali nitrates apparently leads to the formation of basic lead azide as an impurity. If alkali nitrate melts containing precipitated lead azide crystals were left standing for long periods in open containers, moisture was taken up from the atmosphere and the lead azide reacted slowly to form basic lead azide which was identified by X-ray analysis.[4] In order to achieve the highest possible purity not only the crystal growing but also most of the 60 performed precipitations were carried out in a high-vacuum system. A schematic representation of this apparatus can be seen in a previous paper.[5] The precipitations were carried out by dropping finely divided lead nitrate powder from glass spoons, which were rotatable by means of ground joints, into well dehydrated and outgassed alkali nitrate melts containing an alkali azide. The temperatures of the melts during precipitation and crystal growth ranged from 140 to 250°. The chosen temperatures could be kept constant by a temperature-regulated metal block as furnace. Lead azide crystals from 5 to 10 mm in length could be grown in the course of 1–2 days in the vacuum system. Transparent single crystals as well as dendritic growth were found.

The lead azide samples were analyzed for azide content by titration with standard ceric solution, and for lead content, by gravimetric and polarographic methods. Flame emission and microcolorimetric tests indicated that less than 50 ppm of potassium and sodium, less than 5 ppm of lithium, and less than 14 ppm of nitrate were present. Traces of silicon, calcium, and magnesium were found. These results show that very little uptake of ions from the molten salt solvents took place.

Properties and Stabilities of Lead Azide Prepared in Molten Salt Media

The lead azide samples were studied with a Debye–Scherrer camera and with an X-ray diffraction spectrometer. Sharp reflections characteristic of the α form of lead azide were always found. The same d values were obtained with lead azide precipitated in molten alkali nitrates and with lead azide precipitated from aqueous solutions. These d values were also found for powders obtained by crushing large lead azide crystals which were grown from molten salts, as well as from aqueous solutions. None of these four kinds of lead azide powder samples gave an X-ray reflection corresponding to a d value of 5.01 A and having a relative intensity of 40%, such as listed in the literature.[6] The half-widths of the X-ray reflections were measured for a considerable number of lead azide samples. Consistently smaller half-widths were found with samples prepared in molten salt media. Also, very weak X-ray reflections were resolved better with melt-prepared lead azide. These observations indicate an improved structure of lead azide prepared in molten salts.

The thermal stabilities of the various lead azide preparations were studied with a Du Pont micro-dta apparatus using a heating rate of 20°/min. At characteristic temperatures, sharp breaks in the exothermic rise of the dta thermograms occurred which were caused by the increase in heating rate due to self-heating. After a short self-heating period the samples exploded. The temperature where self-heating began may be called the beginning of appreciable decomposition and was determined for a large number of lead azide samples. Consistently higher decomposition temperatures were found with lead azide samples prepared in molten salt media. This can be seen in Table I, where the term microscopic crystals refers to lead azide batches of fairly homogeneous particle sizes which differ from batch to batch in the range 5–100 μ. The macroscopic crystals were 1–5 mm in length. Similar results were obtained with a macro-dta system which permitted the use of 0.5 g of lead azide samples which were subjected to a heating rate of 1°/min. The results displayed in Table I indicate that melt-prepared lead azide has a higher thermal stability. The difference in thermal stability is most pronounced with large crystals.

TABLE I

TEMPERATURES (°C) OF THE BEGINNING OF APPRECIABLE DECOMPOSITION

	PbN_6	
	Prepared in water	Prepared in melts
Microscopic crystals	305–324	336–354
Macroscopic crystals	300–305	340–354

An attempt was made to find out whether or not the thermal stability of lead azide was affected if it was precipitated in concentrated aqueous solutions of alkali nitrates. The lead azide samples prepared in this way did not show higher thermal stabilities than lead azide prepared in alkali nitrate free aqueous solutions.

Lead azide made in molten salts also proved to be more stable in dissolution experiments than aqueous-prepared lead azide. The comparison of samples with the same particle sizes showed that lead azide prepared in molten salt media took at least 3–4 times as long for dissolution in 0.7 and 1.4% nitric acid. In the case of large precipitated crystals the difference in dissolution velocity was considerably larger. These tests were performed in macroscopic experiments as well as by optical microscopy.

This paper shows that azides can be prepared at elevated temperatures using molten alkali nitrates as media. The melt-prepared lead azide decomposed at higher temperatures and dissolved more slowly in dilute nitric acid. All of this is probably due to an increased perfection of the crystal lattice which was indicated by X-ray diffraction work.

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