formed in substantial amounts in the reaction of O_2F_2 with SO_2, the OF radical is probably not an intermediate in the reactions of O_2F_2. The conclusion that the OF radical is not an intermediate in the chemistry of O_2F_2 is substantiated by the fact that OF_2 is not formed in the decomposition of O_2F_2.

Experimental Section

System for Handling O^{17}.—Since the enriched oxygen is very expensive, a method was needed for quantitatively transferring the gas in the vacuum system. Since oxygen exhibits a vapor pressure of approximately 158 mm at $-196°$, it cannot be fully condensed at this temperature. The pressure can be lowered in two ways: either the temperature can be lowered, or the oxygen can be absorbed on a substrate. At liquid helium temperature, the vapor pressure of oxygen is negligible; however, the use of liquid helium is inconvenient and time consuming. The pressure of the absorbed oxygen on Type 13X Linde Molecular Sieves at $-196°$ was found to be less than 0.01 mm when the weight ratio of molecular sieves was 10:1 or greater.

Mass spectral analysis of the oxygen before and after condensation showed that there was no exchange of the enriched oxygen with the oxygen in the molecular sieves.

It was found that the enriched oxygen as obtained from the supplier contained about 3 mol % hydrogen, which would create a serious problem if it were not removed. A convenient method for removing the hydrogen was to condense the bulk sample of gas at 196° in a molecular sieve trap and pump out the hydrogen.

Preparation of O_2F_2.—O_2F_2 was prepared by using the method previously reported.[1] The O_2F_2 enriched in O^{17} was made by using 10% enriched oxygen (YEDA Research and Development Co. Ltd.) in place of ordinary oxygen.

Preparation of Labeled Sulfur Dioxide.—Enriched SO_2 was prepared by allowing sulfur to react with 10% enriched oxygen at 300°.

Reaction of O_2F_2 and SO_2.—After the O_2F_2 was prepared, it was allowed to drain to the bottom of the reactor. A measured amount of SO_2 was distilled into the reactor while the O_2F_2 was maintained at liquid nitrogen temperature. The liquid nitrogen dewar was slowly lowered, allowing the SO_2 to melt and make contact with the O_2F_2. If a solvent was used, it was also distilled into the reactor and used to wash down the reactants. The reactor was then maintained at the desired reaction temperature until the red color of the O_2F_2 disappeared.

Product Analysis.—The reactor was kept at $-196°$ (all of the products except O_2 and F_2 are nonvolatile at this temperature). The O_2 and F_2 formed were allowed to pass through a sodium chloride trap maintained at 200° (the F_2 is converted to Cl_2), through a liquid nitrogen trap to condense the Cl_2 formed, and into a molecular sieve trap maintained at $-196°$ in order to recover the oxygen. The chlorine and oxygen were measured by pressure determination in a calibrated volume.

The remaining products were then separated by trap-to-trap distillation or the Cady[13] codistillation method. The FSO_2OSO_2F, FSO_2OOF, and SO_2F_2 were recovered at -95, -126, and $-160°$, respectively. Both infrared and nmr analyses were used to characterize the products, but F^{19} nmr analysis was the best method, since the chemical shifts for all compounds in question had previously been reported.[14]

Nmr Spectra.—The O^{17} nmr spectra were obtained at 8.13 Mc with the conventional Varian DP-60 equipped with a low-temperature, wide-line dewar coil. The cooling system was altered slightly to obtain better temperature control and to allow rapid insertion of the sample. Gaseous nitrogen that had been previously cooled by passage through a copper coil immersed in liquid nitrogen was used for cooling. The temperature was controlled to within ±1° by varying the flow of nitrogen.

The spectra of F_2SO_2, FSO_2OOF, and FSO_2OSO_2F were obtained at -100, -10, and 25°, respectively. The O^{17} chemical shifts are given with respect to H_2O^{17}. Since it was not possible to use an internal standard for the calculation of chemical shifts, the magnetic field was calibrated before and after each experiment. In the case of high resolution, intensity ratios were computed by integration of signal areas. The F^{19} spectra were observed at 56.4 Mc.

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Explosion Temperatures of Lead Azide Crystals in Molten Salt Environments

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Lead azide crystals which usually explode at temperatures below 320° have minimum explosion temperatures of 500° when dropped into molten alkali halides and 620° when dropped into molten alkali nitrates. Calculations indicate that the high explosion temperatures observed in molten salts may be due to the greatly improved conditions for heat transfer to the surroundings. In alkali nitrate melts lead oxide is formed instead of catalytically acting lead metal which may be the cause for the further increased explosion temperature.

Introduction

The isothermal decomposition of lead azide, $PbN_6 \rightarrow Pb + 3N_2$, is a slow process at temperatures as high as 280°.[2] Nevertheless, raising the temperature of the apparatus only 20–40° is sufficient to cause explosions. This happens because the decomposition rate attains a critical value beyond which no equilibrium between the rate of heat production and rate of heat loss is possible. Self-heating results which leads to explosion.

In experiments not previously reported by this investigator, the temperature increase due to self-heating was

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observed using a Du Pont micro dta apparatus. At characteristic temperatures, sharp breaks in the exothermic rise of the dta curves occurred which were caused by the increase in heating rate due to self-heating. Thereafter, the temperatures in the small glass tubes containing the lead azide samples rose rapidly 30–60° above the programmed temperature of the apparatus and subsequently explosions occurred. Considering the poor conditions for heat transfer from the bulky lead azide crystals to the thermocouple of the dta apparatus and the short time available for the heat transfer, it can be assumed that individual crystals of lead azide attained higher temperatures than the observed over-all temperature increase indicated.

The temperature where self-heating begins can be expected to be dependent on the size of the decomposing crystals and the thermal conductivity of the medium surrounding them. In accordance with this, lower minimum explosion temperatures were found with larger crystals of lead and cadmium azides than with smaller ones.[3–5] Not much attention has been paid to the effects of the medium surrounding the crystals. Under vacuum, lower explosion temperatures were observed than in air.[2b] When lead azide was wetted with high-boiling organic liquids such as dibutyl phthalate, slightly increased minimum explosion temperatures were found[5,6] Similar observations were made in this work with lead azide crystals submerged in silicon oil. However, all of these liquids have low thermal conductivities and may vaporize around the hot lead azide crystals. Inorganic molten salts have considerably higher thermal conductivities and much lower vapor pressures. On the basis of these considerations, an investigation was undertaken to determine the minimum explosion temperatures of lead azide crystals in inorganic molten salt media.

Experimental Section

Most of the lead azide crystals used in this work were grown from solutions of chemically pure, precipitated lead azide in aqueous ammonium acetate. Some were prepared in a molten eutectic mixture of potassium nitrate and lithium nitrate as described previously.[7] The crystals used were 2–4 mm long and approximately 1 mm thick. For the determination of the minimum explosion temperatures test tubes containing the molten salts were placed in vertical wells of a temperature-controlled metal block. Individual crystals were dropped from a height of 80 cm through a guiding glass tube into the molten salts. At least five experiments were conducted at a particular temperature. The temperatures were raised in 10° steps until explosions were observed by their mechanical and acoustical effects. In order to see the crystals during decomposition, these experiments were also carried out in test tubes which were heated with a Bunsen burner. In this case the temperatures were monitored with a thermocouple which was, except for a thin-walled glass tube, in direct contact with the melt. All of the molten salts were prepared from certified reagents dried at 140°. The melts were further dehydrated by bubbling dry nitrogen through them.

For the study of the thermal decomposition of lead azide in molten salt media a high-vacuum decomposition apparatus was used which was shown in a previous paper.[8] Weighed lead azide crystals were placed on spoons having ground joints for attachment to the apparatus. After outgassing, the crystals were dropped into the reaction vessel containing the molten salt by rotation of the spoon at the ground joint. The temperatures of the reaction vessel were kept constant by a temperature-controlled metal block. The decomposition was followed by automatically recording the increase in pressure as measured by an Alphatron gauge. A cold trap was inserted between the decomposition vessel and the Alphatron gauge to remove condensable gases if desired. A bulb for collecting gas samples for mass spectrometric analysis was attached to the apparatus.

Results and Discussion

Molten alkali nitrates do not dissolve lead azide and have been used as media for its preparation at temperatures between 140 and 250°.[7] For determining the minimum explosion temperatures in these media, lead azide crystals were dropped into the molten eutectic mixtures of potassium and sodium nitrates or into molten potassium nitrate. At temperatures up to 350° the crystals came to rest on the bottom of the test tube and formed small bubbles of nitrogen at a low rate. No blackening of the crystal surface due to lead metal formation, often seen in the decomposition of lead azide, was observed. At higher temperatures the lead azide crystals floated, together with the nitrogen bubbles, toward the surface of the melt and decomposed while moving around constantly. Above 500° the lead azide decomposed rapidly forming red clouds of lead oxide. However, no explosion occurred up to 620°. At temperatures above 620° crackling sounds, splashing of molten salt up into the guiding glass tube, and detonations or glass breakage occurred.

The thermal decomposition of lead azide in molten alkali nitrates was studied using the procedures previously outlined in the Experimental Section. When the lead azide crystal fell into the melt, a short outburst of nitrogen occurred. After this, a rather slow first-order reaction followed. For instance, at 458° the half-life of this first-order process was 42 min.

In alkali halide melts such as the low-melting eutectic mixtures of potassium chloride or rubidium chloride with lithium chloride, lead azide dissolves very well. This solubility is probably due to the formation of complexes as was found with lead halides in alkali halide melts.[9–11] The decomposition curves showed that the rate of decomposition was comparatively fast during the few seconds in which the lead azide crystals dissolved. At the end of this period an abrupt change in decomposition rate occurred after which the rate decreased until a fractional decomposition of 0.2–0.3. From there on to a fractional decomposition of about 0.8, the decomposition followed the first-order law.

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This first-order decomposition process was quite slow and had a half-life of 67 min at, for instance, 428°.

The minimum explosion temperatures of lead azide in these alkali halide melts were also studied. The crystals were seen to penetrate into the melts then turn around and float toward the surface where they dissolved within a short time. Below 500° lead azide decomposed without exploding. Above 500°, crackling sounds were heard and detonation as well as spattering of blackened molten salts and frequent glass shattering occurred. Subsequent X-ray analysis indicated that lead metal was formed. The minimum temperature for explosion was not only considerably lower than in alkali nitrate melts but the explosions were also definitely more violent.

Eyring, *et al.*,[12] calculated the time required to reach temperature equilibrium when a particle of 100 μ is immersed in a temperature bath. These authors showed that a surface layer of 1-μ thickness reaches the bath temperature after 10^{-6} sec and the whole particle after less than 10^{-2} sec. These are very short times compared with the observed intervals necessary for dissolution of the crystals. It may be concluded that the lead azide crystals have sufficient time to heat up and explode before they can dissolve. Furthermore, it seems rather unlikely that lead azide in the dilute solution in an alkali halide melt could explode.

The high explosion temperatures of lead azide crystals in molten salt media can be understood if the conditions of heat transfer from the crystals to the medium are considered. In the usual explosion temperature tests the crystals are dropped on surfaces of metal blocks, the temperatures of which are measured. Owing to the roughness of the crystal surface only very small portions of the crystals come in direct contact with the hot metal surface. Air spaces remain in between and most of the crystal surface is still surrounded by air. Therefore, much of the heat generated by the exothermic decomposition has to be dissipated through air which is a very bad heat conductor. When a lead azide crystal is immersed in a melt of alkali halides or nitrates, most of its surface is in direct contact with these media which have 2–3 orders of magnitude greater thermal conductivities than air. Since the lead azide crystals are moving around in the molten salts, heat transfer by convection will also be greater than under the conditions of the usual explosion temperature tests. An attempt was made to look at the relation between thermal conductivity of the medium and the temperature of explosion in a more quantitative way. The temperature was calculated which was necessary for raising the decomposition rate of lead azide to a level where the increased heat loss by conduction in molten salts was compensated. The literature values of the heat conductivity of air and of the heat conductivities of molten alkali nitrates and halides, which are very similar, as well as the reported data on the activation energy for decomposition of lead azide, were used in this calculation.[2,13–16] The activation energy values in the literature vary between 37 and 47 kcal/mole. Using 37 kcal/mole the calculation showed that a temperature of 320° in air corresponds to a temperature of 437° in the molten salt media. With an activation energy of 47 kcal/mole the latter temperature is 408°. These calculations indicate that the better conditions for heat transfer can account for a large part of the increase in the minimum explosion temperatures found in molten alkali halides. Heat loss by convection which was not included in the calculations may bring the point of temperature equilibrium near the temperatures where explosions were observed. A true explosion temperature of lead azide may be 500° as compared to the usual explosion temperatures which are the minimum temperatures of the test apparatus at which explosions occur. In this context it is interesting that Bowden, *et al.*,[17] found in friction tests that only *grit* particles which melt above approximately 500° sensitize lead azide. These authors concluded that temperatures of at least 500° are necessary in localized areas—the so-called hot spots—for initiation of lead azide. From the above calculations it appears likely that considerations based on heat transfer are sufficient to explain the increased explosion temperatures of lead azide in molten alkali halides where the normal reaction products, lead metal and nitrogen, are formed. In alkali nitrate melts considerably higher explosion temperatures were found, and the explosions were less destructive. This may be due to the different reaction path in alkali nitrate melts where lead oxide is formed instead of lead metal which is known to accelerate the decomposition of lead azide autocatalytically.[2,16,18,19] It seems surprising that a reaction which is so fast as the explosion of lead azide should be influenced by the oxidizing properties of the medium. However, it must be kept in mind that the decomposition of lead azide begins at the surface of the crystals and that explosions are preceded by delay times.[2,16,18–20]

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