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EFFECT OF ADSORBATES ON TIME OF THERMAL INITIATION OF LEAD AZIDE

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ABSTRACT

The time of thermal initiation to explosive decomposition of polycrystalline lead azide was studied as a function of interacting proton- and electron-donor vapors at the surface interface. Di- and n-propyl amine as electron donors, and formic and acetic acids as proton donors, changed the time of initiation by approximately plus and minus 25%, respectively. The incremental changes in the times appear to be in the order of the corresponding strengths of the basic and acidic properties of the adsorbates. The adsorbate interactions are interpreted as inducing changes in the population of lead nuclei on the surface of lead azide. The changes in time of initiation are attributed to the fraction of the surface covered by the lead–lead azide interfaces which catalyze the process of lead azide free radical formation leading to explosive decomposition. These results are consistent with the concept that the thermal initiation of lead azide can be surface-catalyzed.

INTRODUCTION

The thermal decomposition of high energy solids initiated by surface processes are usually characterized by an induction period involving the propagation of a chain reaction leading to explosion. Conceivably, the induction period can be shortened significantly by surface adducts which act directly or indirectly as catalysts. The quantity of adduct introduced may be so small that the thermal transport parameter of the substrate surface is affected only negligibly, yet marked influences may be exerted on the chemical processes occurring during the induction period. This can be attributed to the ability of the surface adducts to enhance the concentration of transients necessary for the initiation of chain reactions. However, no direct evidence at monolayer coverages of such adduct interactions with substrate surfaces of primary explosives has been reported in the literature.

One possible manner in which the effects of surface adducts on the induction period can be studied is by exposing the high energy substrate to various interacting vapors (adsorbates) at the onset of thermal initiation. For this purpose a modified explosion temperature apparatus and procedure[1] was used. This paper describes changes in the time of initiation to explosive decomposition induced by various adsorbate–lead azide substrate interactions during the induction period. Electron and proton donor adsorbates were selected on the basis of providing some insight into the relative importance of the postulated electron transfer, free radical, or lead nucleation processes occurring at the surface of lead azide[2-6].

EXPERIMENTAL

Preparation of polycrystalline alpha lead azide

Reagent grade lead nitrate (5.94 g) was dissolved in water 50 cc, cooled, and added slowly to a rapidly stirring solution of reagent grade sodium azide (2.3 g) in water (100 cc), cooled to 0–5°C. The precipitate was allowed to settle and then filtered using a Buchner funnel and Whatman No. 42 paper. It was washed four times with water and twice with acetone, and subsequently dried overnight in a vacuum oven kept at 60°C. The surface area of several batches prepared this way, measured by low temperature krypton adsorption, was 2.1 ± 0.1 M^2/g. All batches were stored in a light-proofed evacuated desiccator.

Vapors and gases

The water used was distilled water, redistilled from alkaline permanganate and sulfuric acid, followed by a third redistillation. The water (as well as all other liquids) was finally degassed by freeze-thawing under vacuum at −78°C.

Argon and krypton were Baker's research grade; sulfur hexafluoride was Air Products C.P. Grade.

Baker's grade acrolein, n-propylamine, dipropylamine, carbon tetrachloride, acetic and propionic acids were kept anhydrous with calcium sulfate. Formic acid (99%) was from K & K Laboratories. It was kept dry over calcium sulfate.

Preparation of hydrazoic acid

An excess of polyphosphoric acid was placed into one arm of a Y-tube. The weight of sodium azide calculated to produce the requisite pressure of hydrazoic acid was placed into the other arm. The charged tube was attached to a vacuum line and degassed overnight with occasional gentle heating of the acid. Generation and subsequent dosing of the hydrazoic acid was carried out by rotating the Y-tube so as to allow the polyphosphoric acid to flow onto the sodium azide. Gentle heating was necessary to speed up the reaction until the calculated pressure was reached. The hydrazoic acid generated in this manner was analyzed mass spectrometrically and found to be free of any detectable quantities of contaminants.

The aluminum capsule-gas assemblies containing hydrazoic acid were sealed in the manner described elsewhere[2]. The excess hydrazoic acid remaining in the vacuum line after each run was neutralized by reaction with a solution of ceric ammonium nitrate.

Adsorption measurements

A BET-type adsorption apparatus, equipped with stainless steel bellows valves, was used to measure the surface area of lead azide with krypton at −196°C. Pressures were read with a Baratron micromanometer having a sensitivity of ±0.001 torr. This apparatus was also used to obtain the adsorption isotherms of n-propylamine, dipropylamine, acrolein, and carbon tetrachloride on lead azide.

Explosion temperature determinations

The procedure used for the containment of vapors and gases in contact with the explosive during the induction period (detailed in a previous publication[1] is described briefly, as follows:

An aluminum capsule was loaded with 40 ±1 mg of lead azide. A slip-fitting teflon plug was inserted into the capsule for consolidating and confining the explosive charge. The annular space resulting from the loose-fitting plug was sufficient to allow free diffusion of vapors to the consolidated explosive charge. The capsule loaded in this fashion was then coupled to a pyrex glass flame-seal tubing by means of a metalized epoxy cement. The resultant aluminum capsule–glass assembly was attached to a vacuum line manifold with Swagelok fittings. The manifold–sample system was evacuated to 10^{-5} torr overnight, dosed with vapors, and prior to flame-sealing the assembly unit, the vapors were condensed into the bottom of the capsule with a liquid N_2 bath to prevent pyrolysis. Before test firing, the aluminum capsule was crimp-sealed hermetically at the section behind the teflon plug. The aluminum capsule–glass assembly was then immersed in a metal bath, heated to the desired temperature, and the time to explosion was determined electronically.

Ultraviolet irradiation

Lead azide (3 g) was contained in a 25-cc vycor ampoule equipped with a stainless steel valve. The sample was degassed on a vacuum line at ambient temperature for 24 h, then placed in a barricaded hood and irradiated with a low-intensity ultraviolet lamp at 2537 Å for five days; it was mixed intermittently to produce a uniform exposure. The evolved gas was analyzed mass spectrometrically and found to be nitrogen with no other detectable constituents.

RESULTS AND DISCUSSION

The time of initiation to explosive decomposition, (t) at a particular temperature may be called the induction period. The relationship between t and the explosion temperature, T, is given by the Arrhenius-type expression in Eqn. (1)

$$t = c\,e^{E_a/RT} \tag{1}$$

where E_a is an apparent activation energy (kcal/mole), so called because the entire explosive sample is not subjected simultaneously to isothermal heating; c is a constant dependent upon the experimental geometry and the composition of the explosive;

T is the explosion temperature in °K; and R is the usual gas constant. The relationship given by Eqn. (1) can be represented conveniently in the logarithmic form:

$$\ln t = \ln c + E_a/RT \qquad (2)$$

The plot of the data, fitting Eqn. (2) gives a linear relationship which summarizes the results for a particular experiment.

The data obtained from the explosion temperature test was programmed into a computer, and the equation of the straight line determined by the method of least squares. Each curve was generated from approximately eight determinations each at five temperatures; and the 95% certainty of displacement on the average for two standard deviations was found to be ±0.12 sec at the high- and ±0.2 sec at the low-temperature regions. The changes in the times of initiation as signified by the displacements of the curves above and below a reference standard curve (a run carried out *in vacuo*) correspond to the desensitization and sensitization of lead azide, respectively.

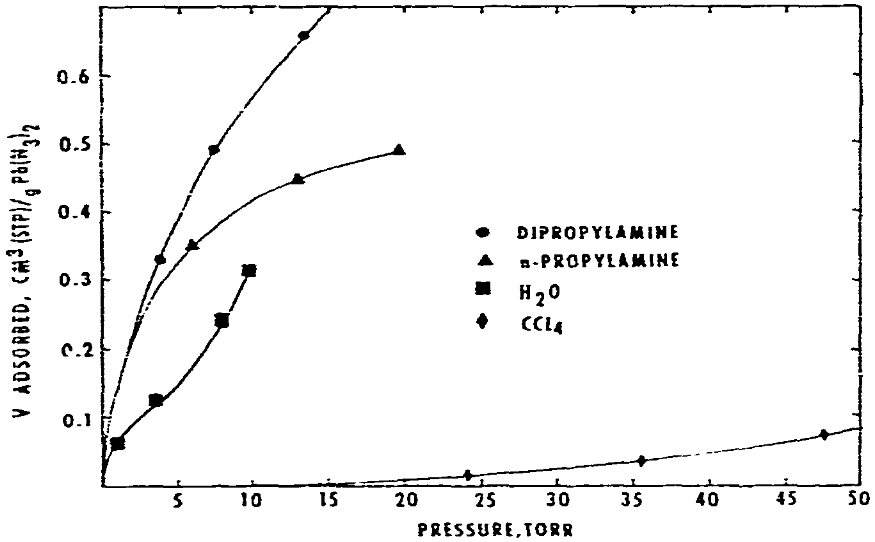

Fig. 1. Adsorption isotherms of vapors on lead azide in the low-pressure region, $t = 25$°C.

Adsorbate–lead azide interaction

The selection of vapors for this study was based on their capability to function as shown in Table I. Also shown in that Table are the types of interaction of these vapors with the surface of lead azide derived from adsorption isotherms, which were determined, not only to indicate the strength of physical adsorption, but also to furnish the equilibrium pressures corresponding to monolayer coverages. Fig. 1 shows the low-pressure region of isotherms (plots of amount adsorbed against equilibrium pressure at 25°C) for n-propylamine (NPA), dipropylamine (DPA), water and carbon tetrachloride on lead azide. The isotherms of NPA, DPA and water are type II, which is indicative of relatively strong physical adsorption. The isotherm for CCl_4 is type III, indicative of weak adsorption, where the heat of adsorption is approximately equal to the heat of vaporization of the bulk adsorbate.

TABLE I

CLASSIFICATION OF ADSORBATE–$Pb(N_3)_2$ ACTIVITY

Adsorbate	*Isotherm type*	*Interaction*	*Function*
n-Propylamine	II	strong, physical	electron donor
Di-propylamine	II	strong, physical	electron donor
Acrolein	II	moderate-strong, physical	radical scavenger
Acetic acid		chemical	proton donor
Propionic acid		physical-chemical?	proton donor
Formic acid		chemical	proton donor
Carbon tetrachloride	III	weak physical	electron scavenger
Argon		none	inert
Sulfur hexafluoride		none	electron scavenger
Water	II	moderate-strong, physical	proton donor

The adsorption isotherms for formic, acetic, and propionic acids and acrolein were determined only to a limited extent. The acids showed varying degrees of incipient chemical reactivity; and acrolein exhibited a tendency to polymerize in the electronic section of the pressure gauge. Despite these limitations, the types of adsorptive interaction could be determined. They are listed in Table I.

TABLE II

PRESSURE[a] OF VARIOUS VAPORS/GASES IN CONTACT WITH ADSORBATE AND/OR SUBSTRATE INTERFACES

Vapor/gas	P[b]	*Vads* [cm^3 (*STP*)/*40 mg*]	P_{eq}[c]	P_{des}[d]	P_{total}[e]
n-Propylamine	293	0.02	20	691	1441
Di-propylamine	20	0.03	20	829	1720
Argon			250		552
			600		1324
Sulfur hexafluoride			250		552
Acrolein	300	0.01	15	304	648
Carbon tetrachloride	100	0.003	50	83	278
Acetic acid	15	0.006	10	166	358
Propionic acid	5	0.003	5	83	179
Formic acid	40	0.003[f]		83	179
Hydrazoic acid			10		>23
			20		>46
Water	20	0.007	6	19	51

[a] All pressures are given in torr. [b] Pressure of vapor in equilibrium with liquid at 23 °C. [c] Pressure in equilibrium with adsorbate at 23 °C. [d] Calculated pressure based on complete desorption of adsorbate at 50 °C. [e] $P_{total} = P_{eq} + P_{des}$, based on free space volume, 0.03 cc at 650 °K. [f] Released from teflon plug at elevated temperature of bath.

The pressures of the various vapors in equilibrium, and of the gases in contact with the substrate lead azide are listed in Table II. Explosion temperature runs of lead azide in argon at the widely different pressures listed in Table II did not differ significantly from runs made in vacuo; consequently, vacuum runs were used as standards. The pressures of the various vapors and gases were in the range of those of argon. Hence, any observed deviation in the rates was attributed to chemical interaction and not to a pressure effect.

The curves in Fig. 2 show an increasing downward shift (sensitization) of lead azide with age. After twenty weeks the curve appears to remain constant. Since aging seems to influence the time of initiation of lead azide all experimental runs were compared with vacuum curves determined within a few days of the particular experiment.

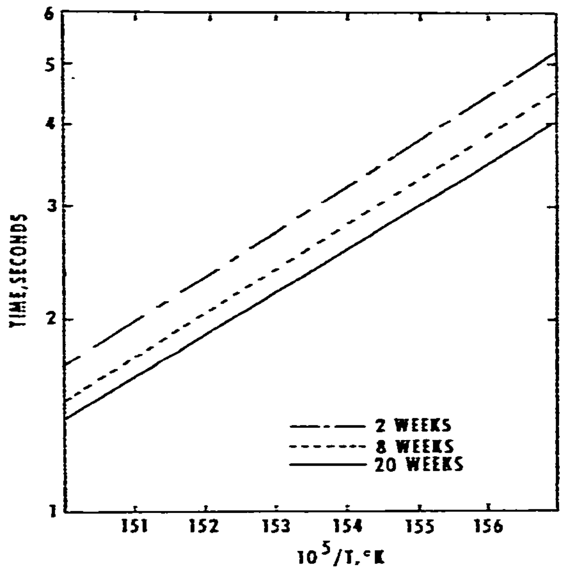

Fig. 2. The thermal explosive decomposition of lead azide as a function of time.

Vapors and gases producing no effect

Times of initiation of lead azide exposed to acrolein, propionic acid, carbon tetrachloride, sulfur hexafluoride and water did not differ significantly from the standards. Water, having amphoteric properties, could act as either an electron donor or acceptor. However, the activation energy must be too high for incipient reactivity with lead azide during the induction period. In the case of acrolein, the electron affinity of the carbonyl group might not be sufficiently high to interfere with any of the electron transfer processes. In spite of its ability to act as a radical scavenger, due to the unsaturated linkage, the reactivity of the azide radical to form nitrogen is too rapid for acrolein to act in this capacity. Because CCl_4 and SF_6 exhibit little or no adsorption on lead azide, their residence time is too short to allow them to function as classified in Table I, at the elevated temperatures during the induction period. Although propionic acid adsorbs strongly on lead azide there was no indication of chemical reaction at ambient temperatures. This would suggest that the rate of reaction with lead azide is too slow for instantaneous participation in the surface processes during initiation.

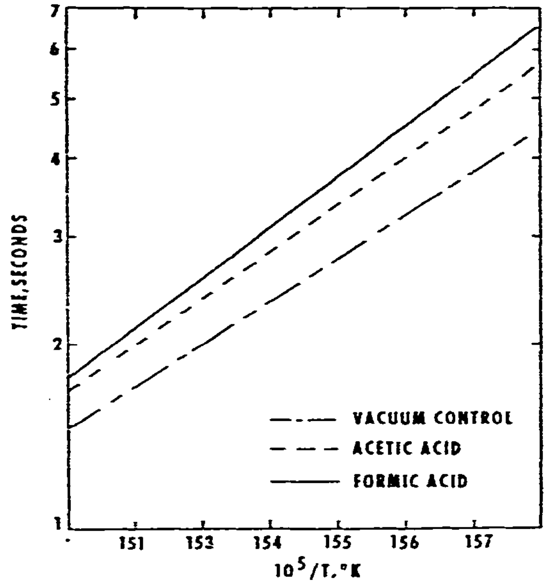

Fig. 3. The thermal explosive decomposition of lead azide exposed to proton-donor vapors.

Desensitization by proton-donor activity

The curves plotted in Fig. 3 for lead azide exposed to formic and acetic acids show a significant upward shift indicating a prolongation of the times of initiation (desensitization). The shifts are in the order of the relative strengths of the acids, that is, 36% and 22% for formic and acetic acids, respectively, with no shift for propionic acid. However, because of the incipient reactions indicated by the adsorption isotherms of formic and acetic acids, interpretation of results required further investigation.

The reaction of the acids with lead azide was verified by mass spectrometric analysis. The gaseous reaction product was identified as pure hydrazoic acid in quantitative yield based on the reaction in Eqn. (3).

$$Pb(N_3)_2 + 2RCOOH \rightarrow Pb(OCOR)_2 + 2HN_3 \qquad (3)$$

Formic acid was found to react completely with an excess of lead azide in 20 min; and 10% of acetic acid was depleted at the end of 2 h as determined by the corresponding hydrazoic acid formation.

Since formic acid *per se* was apparently not present during the explosion temperature runs, the prolonged times to explosion could perhaps be attributed to interfaces of lead azide/lead formate, lead azide/hydrazoic acid–lead formate, or lead azide/

hydrazoic acid. Accordingly, assemblies dosed with formic acid were allowed to stand overnight to ensure complete depletion of formic acid (later verified, Table III). In one case, assemblies were sealed with the reaction gas product remaining (lead azide/lead formate–hydrazoic acid); in another, the gas was pumped off prior to sealing (lead azide/lead formate). In a separate experiment hydrazoic acid was dosed into the assemblies containing pure lead azide (lead azide/hydrazoic acid) and then sealed. Contrary to our expectation, no significant difference in times to explosion with respect to the vacuum control was found to exist among any of these systems. It is possible that the electron affinity of the carboxylic group in lead formate is not strong enough to interfere with any chemical process during the induction period. Apparently, the hydrogen ion released in the process of lead formate formation under steady state conditions is an effective scavenger of the azide ion; and the resultant hydrazoic acid present in the vapor phase at pressures in the range of 10–20 torr does not have any effect on the time of initiation of lead azide, whether in contact with lead azide/lead formate or pure lead azide as might have been expected. Nevertheless, the observed desensitization has to be attributed to the formic acid/lead azide interface in spite of its apparent depletion prior to determining explosion temperatures. Thus, attention was given to the possible disposition of the formic acid under the conditions of the experiment.

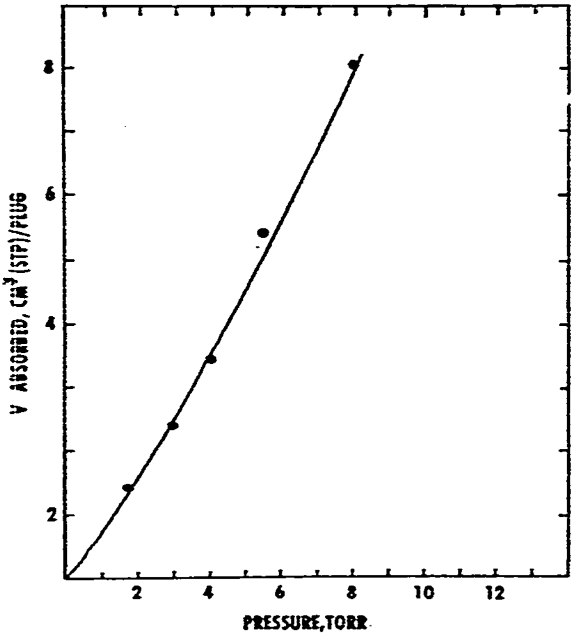

Fig. 4. Sorption isotherm of formic acid in teflon plug at 23 °C.

Since the teflon plug used to seal and confine the explosive is made of compressed and sintered powder, a possibility existed for the formic acid to diffuse into the bulk of the porous plug. An absorption isotherm was determined (Fig. 4), which shows that sorption of formic acid into the teflon plug does indeed occur. Rates of desorption were determined and, as shown in Table III, demonstrate that sufficient formic acid can be desorbed from a teflon plug during the explosion temperature run to account for the decreased time of initiation observed in Fig. 3. For the 40-mg sample of lead azide loaded in each assembly, there are approximately 10^{16} lead azide molecules at the surface. From the desorption data, approximately 10^{17} molecules of formic acid were calculated to be contained in the teflon plug at the onset of the explosion temperature determination. The reactivity of formic acid with the surface of lead azide was shown experimentally to be independent of a lead formate adduct. Successive doses of formic acid to the same sample of lead azide, in a separate experiment, resulted in continued reaction until all of the lead azide was consumed. Therefore, when subjected to elevated temperatures, the teflon plug releases enough formic acid to react effectively with the lead azide surface during the induction period. Supposedly, solely under non-steady state conditions, as prevalent during the induction period, can the scavenging of lead and azide ions by the dissociated acids momentarily delay the buildup of lead nuclei in colloidal aggregates and free radical formation.

TABLE III

DESORPTION OF FORMIC ACID FROM TEFLON PLUG AT 23 °C

Time (h)	*Formic acid remaining in plug [cc (STP) × 10³]*	*Desorbed (%)*
Initial[a]	3.40	
0.6[b]	2.94[c]	13.6
2.1	2.31	32.2
3.9	1.44	57.6
20.0		100

[a] After thawing from −196 °C to 23 °C. [b] Start of explosion temperature test. [c] Equivalent to 4×10^{16} molecules of formic acid interacting with PbN_6 during induction period.

Sensitization by electron-donor activity

The curves plotted in Fig. 5 for lead azide exposed to NPA, DPA and UV irradiation (prior to testing) exhibit a downward shift (sensitization), relative to the vacuum control. As Lewis bases, these amines exert strong forces of adsorption (Fig. 2). Presumably, the stronger the adsorption as a function of basicity, the easier is the release of the unshared pair of electrons, and the longer is the residence time of the amine in the adsorbed state; consequently, the greater is the extent of participation of the adsorbate in the electron transfer processes extant during initiation. These interdependent relationships are borne out by the fact that DPA, as the more basic of the two amines, adsorbs more strongly than NPA on lead azide, (Fig. 2); and that there is a greater downward shift of the curve for DPA (24%) than for NPA (19%), Fig. 5.

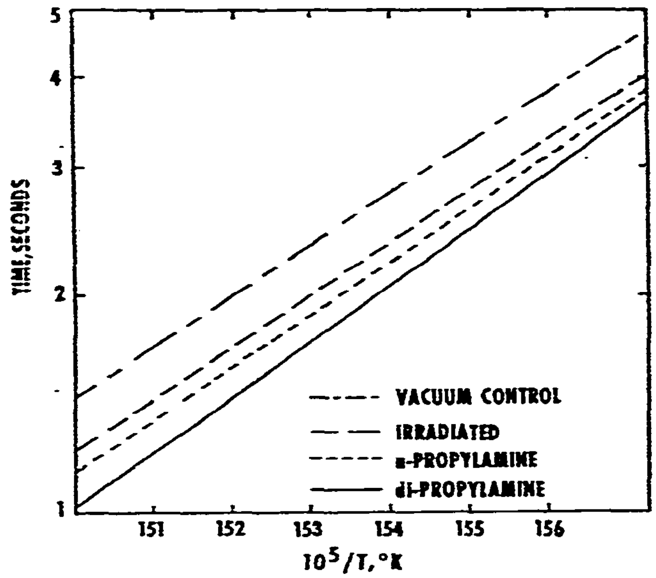

Fig. 5. The thermal explosive decomposition of lead azide exposed to electron-donor vapors.

The UV interaction with lead azide producing lead nuclei is confined primarily to the surface layer representing a few molecular layers thickness. Intimately dispersed in the surface region as relatively non-volatile constituents, ample opportunity exists for these lead nuclei as colloidal aggregates to behave at elevated temperatures as electron sinks which may hasten electron-transfer processes as with the amines) during the non-steady state period; and, thereby, account for the observed shortened times leading to explosive decomposition.

Postulated mechanism of lead decomposition

The stepwise reactions in the postulated mechanism[3] of the explosive decomposition of lead azide may be summarized as follows.

At elevated temperatures, prior to explosion, the equilibrium in Eqn. (4) would be expected to shift to the right

$$Pb(N_3)_2 \rightarrow Pb^{2+} + 2N_3^- \qquad (4)$$

The induction period associated with the decomposition of lead azide may be characterized as the time during which the initial step is the formation of the azide-free radical and nascent lead, as in Eqn. (5)

$$2N_3^- + Pb^{2+} \rightarrow 2N\cdot_3 + Pb \qquad (5)$$

The activation energy, E_a for the formation of free radicals from the azide ion is larger than the E_a for the formation of N_2 by the combination of two azide radicals in adjacent positions at the surface (Eqn. 6).

$$2N\cdot_3 \rightarrow 3N_2 + Q \qquad (6)$$

where Q contributes to the self-supporting reaction leading to explosion; it is reported to have a value of 10.9 eV, or 250.7 kcal/mole. Therefore, the generation of free radicals becomes the rate determining step. As decomposition proceeds, the population of nascent lead increases to form aggregates of lead nuclei at the surface interface, which then act as traps for any freshly formed free electrons and lead ions (Eqn. 7).

$$2N_3^- + Pb^{2+} + Pb_n \rightarrow Pb_{n+1} + 2N^{\cdot}_3 \qquad (7)$$

Lead nuclei act as the catalyst for the formation of free radicals from the azide ion at the metal–metal azide surface-interface by lowering the E_a of the rate determining step[4]. At this point auto-catalysis sets in, leading to the self-supporting exothermic decomposition.

Role of adsorbate reactions

The rate of reaction catalysed at the surface depends to a large extent on the fraction of the surface covered by the lead–lead azide interface. The results of the experiments on the sensitization and desensitization of lead azide can be interpreted on this basis.

The amine adsorbates and UV interactions with the surface of lead azide can be considered as effectively enhancing the formation of lead nuclei at the surface interface. The photolytic decomposition of lead azide has been established in the open literature[6], and verified in this work.

$$Pb(N_3)_2 + h\nu \rightarrow Pb + 3N_2 \qquad (8)$$

The postulated ground state molecular charge-transfer complex in Eqn. (9) is based on the reported[8] property of amines to complex with metal salts in the solid state.

$$Pb(N_3)_2 + 2RNH_2 \rightarrow Pb(N_3^- H_2N^+R)_2 \qquad (9)$$

During the initial stage of heating in the explosion temperature bath, the complex presumably disproportionates, releasing nascent lead

$$Pb(N_3^- H_2N^+R)_2 \rightarrow Pb + 2(RN^+H_2N_3^-) \qquad (10)$$

The process of lead nucleation may, thus, be favored by reactions according to (Eqns. 7) and (10) which increase the rate of free radical formation (Eqn. 7). In this manner, the onset of auto-catalysis is hastened, resulting in the observed shorter times to explosion if compared with the vacuum controls.

The observed decrease in times of initiation associated with the *in situ* interactions of the acids with the surface of lead azide could be attributed to the incipient scavenging of lead and azide ions which form non-participating reaction products (Eqn. 3). Not only was the azide ion apparently stabilized in the form of hydrazoic acid, but lead nuclei buildup was momentarily hindered by the concomitant lead salt formation of formic and acetic acids. The overall effect was a temporary repression of the reaction described in Eqn. (7), resulting in the observed delays in the onset of auto-catalysis leading to explosive decomposition.

CONCLUSIONS

There appear to be two criteria which affect the thermal sensitivity of lead azide via adsorbate–adsorbent interaction. One is that the adsorbate be strongly adsorbed. Adsorbates with terminal polar groups such as OH, NH_2 and COOH are attracted strongly by the electrostatic field of a surface[9], accounting for the observed strong adsorption of the amines, propionic acid and water. The other criterion is the tendency of the adsorbate to interact with the substrate as electron and/or proton donors. The residence time for adsorption should be long enough, and the activation energy for interaction low enough, to ensure participation during the onset of the surface processes leading to explosive decomposition.

The approximately ±25% changes in the time of initiation of lead azide by the corresponding proton- and electron-donor reactions represent additional evidence for the postulated process of auto-catalysis as being initiated at the surface. The extent of the enhanced or repressed population of lead nuclei is probably governed by the concentration of the available lead azide surface molecules of the particular sample used in this study.

The proton- and electron-donor adsorbate activity inducing changes in the thermal sensitivity of lead azide were observed to take place during the non-steady state conditions of the induction period. However, the sensitization of lead azide need not be limited to an *in situ* participation of surface reactants during the induction period. Lead azide is photosensitive, and consequently it is contaminated with metallic lead by exposure to light in the normal course of preparation and handling. The UV experiment described in this work, and the evidence cited in the literature[10], indicate that an increase in the lead–lead azide interfaces prior to thermal initiation effectively hastens the process of auto-catalysis and hence, decreases the time to explosion.

The promotion of auto-catalysis by the increased concentration of lead nuclei is suggestive of the importance of lead nuclei contamination of lead azide. The threshold of energy transfer could be unexpectedly high in pure lead azide, initially free of lead nuclei contamination in the bulk as well as at the surface. By the addition of dopants that would desensitize lead azide to UV light and deactivate the lead nuclei already present, it may be possible to obtain a higher threshold energy than is presently required for the initiation of lead azide, if this were indeed a requirement.

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