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A THERMAL STUDY OF THE SALTS OF AZOTETRAZOLE

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ABSTRACT

The four salts of 5,5′-azotetrazole (AzTz) selected for the present study were (1) disodium azotetrazole (Na_2AzTz), (2) barium azotetrazole (BaAzTz), (3) lead azotetrazole (PbAzTz), and (4) mercury azotetrazole (HgAzTz). An attempt was made to correlate the thermal properties of these compounds with their explosive properties. Thermal behaviour was studied by thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques under non-isothermal conditions. Compounds 1 and 2 showed endotherms at 120–140°C and 80–100°C, respectively, and exotherms at 265–315°C and 180–220°C, respectively, whereas compounds 3 and 4 showed only exotherms at 180–210°C and 144–160°C, respectively. The weight losses observed in TG corresponding to the endotherms confirmed that they are due to removal of water of crystallisation. The enthalpies of dehydration and decomposition were calculated from experimental data. The kinetics of dehydration and decomposition were studied. The explosive sensitivity was determined by impact, friction and static charge tests. The thermal and explosive sensitivities increase in the order $Na_2AzTz < BaAzTz < PbAzTz < HgAzTz$. The results indicate a good correlation between thermal sensitivity and explosive sensitivity.

INTRODUCTION

Tetrazole is an interesting molecule with a high nitrogen content. Because of the low carbon content, tetrazole derivatives can easily be oxygen balanced. Most of the tetrazoles decompose/detonate when they are subjected to stimuli like friction, impact, spark, etc., with the liberation of a large volume of gas and a lot of heat. Tetrazole salts such as lead azotetrazole [1], copper nitrotetrazole [2] and tetracene [3] have been claimed for use as primers. The literature survey reveals that the thermal decomposition characteristics of tetrazole derivatives, except that of tetracene [4] and basic lead azotetrazole [5], have not been studied in detail. A systematic study on

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explosive properties of the salts of azotetrazole has not been reported in the literature. Therefore, we have taken up a detailed study on the thermal and explosive properties of salts of azotetrazole.

Thermal analysis of explosive materials can provide information regarding the thermal sensitivity/stability, safety in handling at different temperatures, the mechanism and kinetics of decomposition, the energy of decomposition, etc. In brief, using modern thermal analysis techniques such as TG and DSC, the thermal behaviour of explosive materials may be determined in a short time using milligram quantities. The compounds selected for the present study were: (1) disodium azotetrazole (Na_2AzTz), (2) barium-5,5′-azotetrazole (BaAzTz), (3) lead-5,5′-azotetrazole (PbAzTz) and (4) mercury-5,5′-azotetrazole (HgAzTz).

5,5′-Azotetrazole is not prepared in the free state as it is not stable. Its sodium salt is prepared by oxidising 5-aminotetrazole with potassium permanganate in alkaline medium. Thiele [6] prepared metallic salts of azotetrazole and claimed these for use in initiators. Ruthsburg [7] has taken a patent on Cd and Pb salts of azotetrazole. The author claimed that the impact sensitivity of PbAzTz is more than that of mercury fulminate. However, as mentioned earlier, a systematic study on the explosive properties has not been carried out. Therefore, the explosive properties and thermal characteristics were evaluated in this study.

EXPERIMENTAL

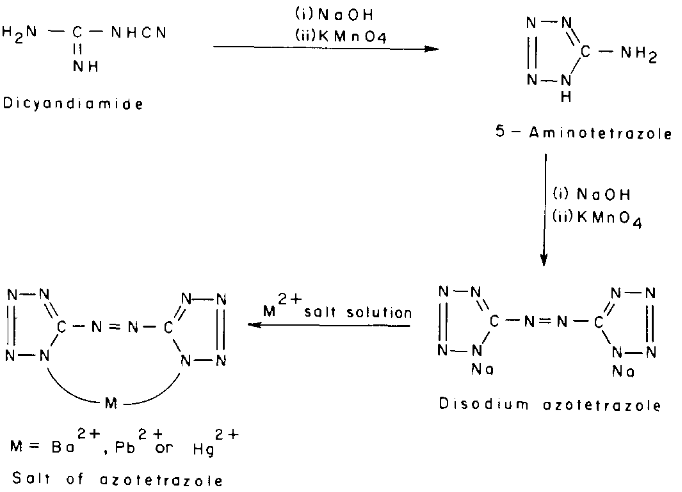
Materials

Preparation of disodium 5,5′-azotetrazole

50 g (0.5 mole) of dried 5-aminotetrazole (5-AmTz) monohydrate was dissolved in 500 ml of 10% sodium hydroxide and heated to 65°C on a water bath. 65 g of potassium permanganate was slowly added to the hot alkaline solution of 5-AmTz while stirring over a period of 30–40 min. Stirring was continued for another 2 h at the same temperature. 500 ml of alcohol (95%) was added to reaction mixture and boiled for a few minutes while stirring. The hot slurry was filtered to remove manganese dioxide. On cooling, the filtrate gave golden-yellow-coloured needles of $Na_2AzTz \cdot H_2O$. The product was washed with a little alcohol and dried at room temperature

Preparation of salts of 5,5′-azotetrazole

A 0.1 M solution of Na_2AzTz was prepared by dissolving in distilled water. The solution was placed in a stainless steel beaker and heated to 60°C on a water bath. A slight excess of a 0.1 M solution of the M^{2+} salts (M^{2+} = barium, lead and mercury) was added dropwise at 60°C while stirring over a period of 5–10 min. It was further stirred for 15 min at the



Scheme 1

same temperature. After cooling to room temperature it was filtered. washed with water first, later with acetone and then dried. When crystal modifiers like dextrin, carboxymethyl cellulose (CMC) were used, the 5% solution was mixed with Na_2AzTz solution before adding the metal salt solution (see scheme 1).

Instruments

A Mettler TA-2000C was used for simultaneous TG–DSC study. The thermograms were recorded under non-isothermal conditions at different scan speeds using an inert gas atmosphere (helium) at a flow rate of 60 ml min^{-1}. All the runs were recorded after standardising the instrument using indium and tin as standards for DSC and copper sulphate pentahydrate for TG. Samples were weighed in aluminium oxide cups (Aloxcrucibles and covers, 0.08 ml, ME-24123) and lids with a hole were placed over the cups. The sample size varied from 0.1 to 0.4 mg for different compounds. Alumina is added as a diluent to the exploding materials (PbAzTz and HgAzTz) and scanned at low heating rates. A Perkin-Elmer DSC-1B was used for delay time measurements. Samples were weighed in aluminium cups and kept open. Experiments were carried out under a nitrogen atmosphere [8].

The IR spectra of the residues after decomposition in TG–DSC were recorded on a Perkin-Elmer 577 infrared grating spectrophotometer in the form of KBr discs.

RESULTS AND DISCUSSION

Thermal properties

Typical TG–DSC thermograms for the decomposition of Na_2AzTz, BaAzTz, PbAzTz and HgAzTz are shown in Fig. 1. Na_2AzTz and BaAzTz are monohydric salts. In the case of the sodium salt the weight loss observed

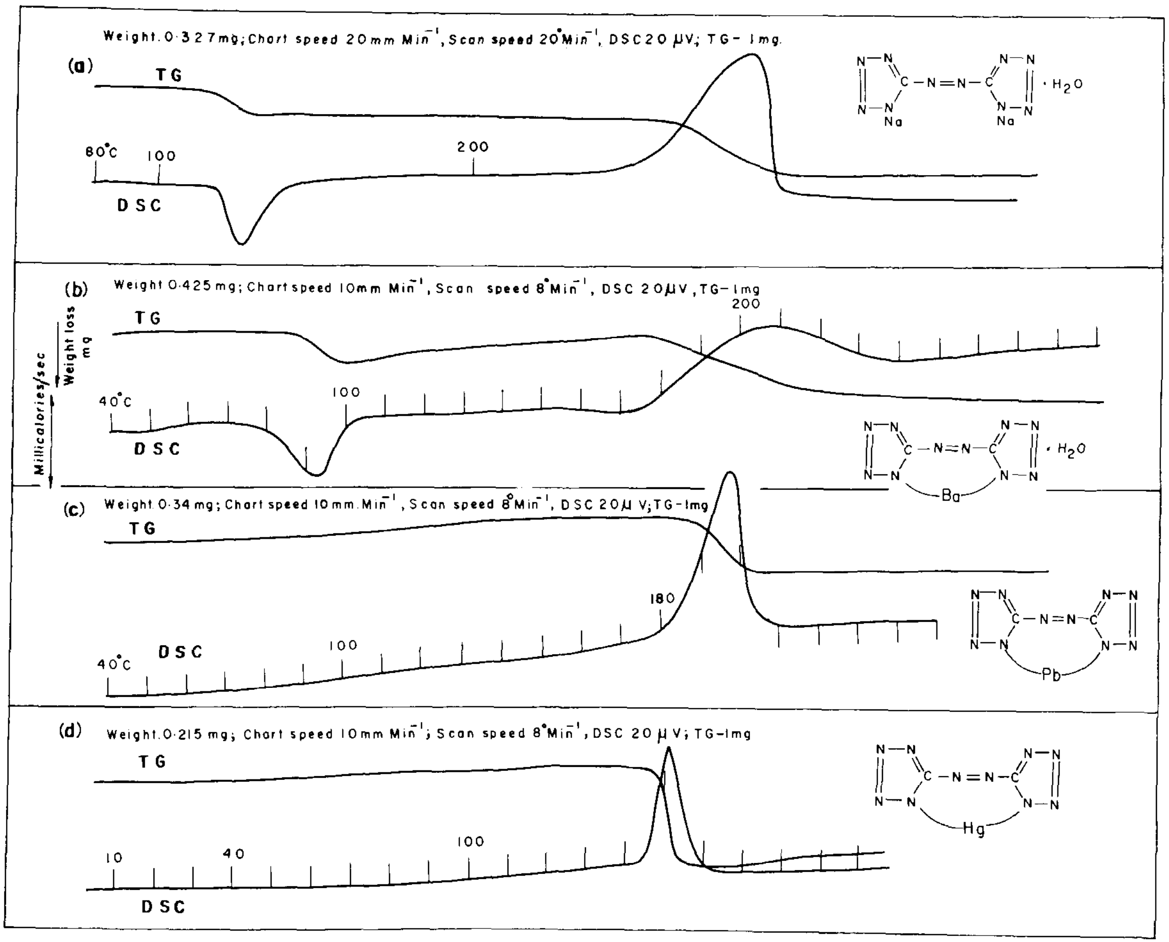


Fig. 1. Typical non-isothermal TG–DSC curves for (a) 5,5′-disodium azotetrazole, (b) barium azotetrazole, (c) lead azotetrazole and (d) mercury azotetrazole.

TABLE 1

ΔH values

Compound	Dehydration (kJ mole^{-1})	Decomposition (kJ mole^{-1})
$Na_2AzTz \cdot H_2O$	96.95 ± 3.8	418.43 ± 11.2
$BaAzTz \cdot H_2O$	126.82 ± 4.2	502.27 ± 12.8
PbAzTz		589.59 ± 15.0
HgAzTz		609.88 ± 14.22

in TG corresponding to the endotherm in the range 120–140°C is 7.1 to 7.2% (theoretical value based on the loss of one water molecule is 7.9%). Therefore, it is concluded that Na_2AzTz is monohydric and loses one water molecule in the temperature range 120–140°C with the absorption of heat as indicated by the endotherm in the DSC curve. The quantity of heat absorbed during dehydration was estimated and is shown in Table 1. The kinetics of dehydration was studied from DSC curves and the activation energy values and order of reaction obtained by least-squares curves fit method are shown in Table 2. The Kissinger shape index method [9], Coats and Redfern method [10], and Borchardt and Daniel [11] method gave n equal to one. The methods of Ozawa [12] and Kissinger [13] gave low activation energies when compared with the other three methods whose values are comparable to each other (see Table 2). The method of Rogers and Morris [14] gave different values for ascending and descending portions of the curves. But the average value is comparable with the values obtained by the Borchardt and Daniel and the Coats–Redfern method. The TG curves were not analysed for kinetic study due to the problem in obtaining the fraction-decomposed values at various temperatures as the sample size was very low (0.2–0.4 mg).

The endotherm in the range 80–100°C for $BaAzTz \cdot H_2O$ is due to the loss of water of crystallisation. The corresponding weight loss in the TG curve is 5.02–6.0% (theoretical value based on the loss of one water molecule is 5.64%). The heat of dehydration is shown in Table 1. From the results of the heat of dehydration and temperature range, it is clear that the removal of one water molecule from the sodium salt is difficult when compared with the barium salt indicating more ionic character and a stronger bonding of the water molecule with the tetrazole molecule. Activation energy values obtained by different methods for dehydration are shown in Table 2. The order of reaction calculated by various methods gave n equal to one. There is a fair agreement between the activation energy values obtained by various methods. Lead and mercury salts did not show an endotherm indicating the absence of water of crystallisation.

The orders of reaction for the decomposition curves derived by various methods using the least-squares curve fit program do not concur, though the

TABLE 2

Activation energies of dehydration, $E_{act.}$, obtained using DSC and the least-squares method

Compound	$E_{act.}$ (kJ mole^{-1}) by the method of				
	Ozawa	Kissinger	Rogers and Morris [a]	Borchardt and Daniel	Coats and Redfern
$Na_2AzTz \cdot H_2O$	173.88 ± 4.2	169.28 ± 3.9	Asc. 452.50 ± 10.5 Dsc. 279.49 ± 8.2 Ave. 365.49 ± 9.4	366.10 ± 10.6 ($n = 1$)	442.66 ± 15.2 ($n = 1$)
$BaAzTz \cdot H_2O$	180.25 ± 6.5	176.50 ± 5.2	Asc. 125.03 ± 5.0 Dsc. 279.70 ± 6.8 Ave. 202.36 ± 5.9	210.30 ± 6.5 ($n = 1$)	228.12 ± 5.0 ($n = 1$)

[a] Asc. = ascending portion of the DSC curve; Dsc. = descending portion of the DSC curve; Ave. = average value.

TABLE 3

Activation energy, $E_{act.}$, and log Z data of decomposition

Compound	$E_{act.}$ (kJ mole^{-1}) and log Z (s^{-1}) by the Method of								
	Ozawa $E_{act.}$	Kissinger $E_{act.}$	Rogers and Morris			Borchardt and Daniel $E_{act.}$	Coats and Redfern $E_{act.}$		Delay time $E_{act.}$
			$E_{act.}$		log Z				
$Na_2AzTz \cdot H_2O$	319.97	312.27	Asc.	237.76	34.24	285.24	Dsc.	382.53($n = 1$)	192.13
			Dsc.	496.96		($n = 1$)	TG	373.47($n = 1$)	
			Ave.	367.36					
$BaAzTz \cdot H_2O$	148.60	144.78	Asc.	154.00	16.01	162.24	Dsc.	218.70($n = 2$)	125.58
			Dsc.	153.20		($n = 2$)	TG	150.86($n = 2$)	
			Ave.	153.60					
PbAzTz	275.31	265.55	Asc.	333.37	42.44	397.37	Dsc.	405.28($n = 1$)	244.25
			Dsc.	485.11		($n = 1.5$)	TG	411.11($n = 0.5$)	
			Ave.	404.24					
HgAzTz	270.03	269.59	Asc.	131.44	17.21	240.10	Dsc.	241.44($n = 2$)	211.81
			Dsc.	166.68		($n = 2$)	TG		
			Ave.	149.06					

Asc. = ascending portion of the DSC curve; Dsc = descending portion of the DSC curve; Ave. = average value.

activation energy values are in agreement (see Table 3). Therefore, the method of Doulah [15] was applied to determine the type of mechanism operating in the decomposition. In the Doulah method a plot of ln ln$[1/(1-\alpha)]$ vs. $\ln(T-T_0)/\phi$ gives a straight line with a slope of β. This method utilises the equation

$$\ln \ln[1/(1-\alpha)] = \beta \ln t + b \ln r$$

when $t = (T-T_0)/\phi$ for dynamic runs. T is the temperature at a given α and T_0 is the inception temperature.

If $\beta = 1$, the decomposition follows first-order decay. If $1 < \beta < 3$, the decomposition occurs at the phase boundary of the products. When $\beta > 3$, the nucleation starts at the boundary and when $\beta < 1$, the gaseous products control the reaction.

The values obtained for β by using the foregoing equation indicate that

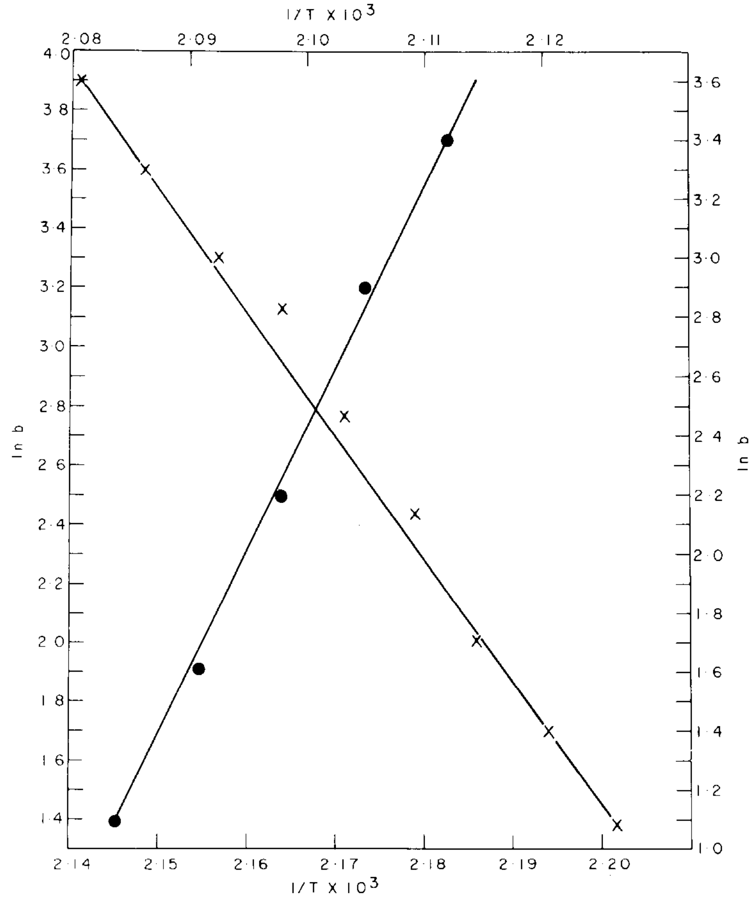


Fig. 2. A plot of the Rogers and Morris method for the non-isothermal DSC analysis of lead azotetrazole. ●, Descending curve, $E_{act.} = 485.11$ kJ mole^{-1}; ×, ascending curve, $E_{act.} = 333.29$ kJ mole^{-1}.

the decomposition occurs at the phase boundary of the products. The α vs. t curves were of sigmoid type. The α vs. reduced time plots indicated the same type of mechanism at all heating rates. A typical Rogers and Morris plot and Coats and Redfern plots for the analysis of DSC curves of lead azotetrazole have been shown in Figs. 2 and 3. The activation energies derived from the DSC decomposition curves of azotetrazoles are shown in Table 3.

An isothermal study was not possible because of the difficulties in recording thermograms at different temperatures. Only a delay time method [16] was employed. In this method the temperature of the sample was increased quickly to the desired temperature by rotating the knob given for Perkin-Elmer DSC 1B. When the required temperature was obtained as indicated by the green light on the programming unit, the stop watch was started and the time required for the explosion, as indicated by the pen movement, was noted. Thus delay time at various temperatures was determined. A plot of ln (delay time) vs. the reciprocal temperature should give a straight line with a slope of $-E/R$. The intercept gives a constant B, as shown in the equation

$$\ln(\text{delay time}) = \frac{-E}{RT} + B$$

Using the delay time method all salts gave low activation energy values (see

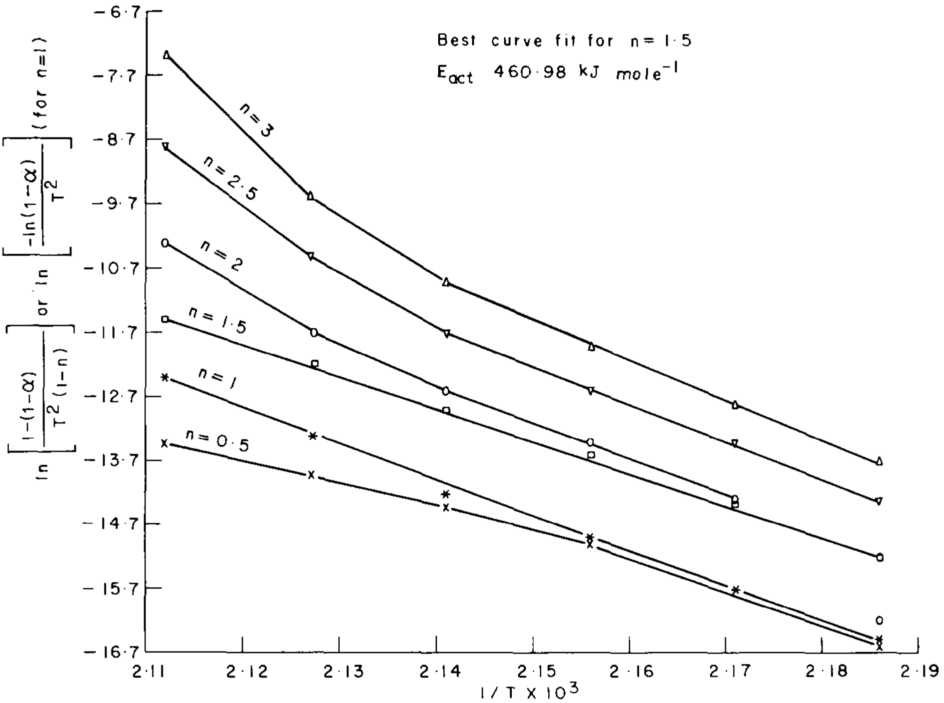


Fig. 3. Typical plots of the Coats and Redfern method for the DSC decomposition curve of lead azotetrazole for various values of the order of reaction.

TABLE 4

Weight losses for dehydration and decomposition observed in TG

Compound	Dehydration[a] (%)	Decomposition[b] (%)
$Na_2AzTz \cdot H_2O$	7.12 (obs.) 7.89 (theo.)	33.66–36.50
$BaAzTz \cdot H_2O$	5.82 (obs.) 5.65 (theo.)	16.20–20.10
PbAzTz		18.49–21.02
HgAzTz		

[a] obs. = observed and theo. = theoretical value based on the loss of one molecule of water.
[b] Decomposition weight loss indicates the loss of N_2 and HN_3 from the tetrazole rings.

Table 3) which were comparable with those given by the methods of Ozawa and Kissinger.

The weight loss values observed in the TG curves, corresponding to decomposition are shown in Table 4. When explosion occurred the weight loss observed was 100%. The weight-loss measurements did not give clear-cut information regarding the mechanism of decomposition. The results only indicate that the tetrazole ring was broken and nitrogen gases were formed. This was further confirmed by the IR spectra of the residual mass. The frequency due to tetrazole was absent. The activation energies for the decomposition of salts of azotetrazole from TG curves were calculated using the Coats–Redfern method. The results are shown in Table 3. Specific heats were calculated and are shown in Fig. 5. The increase in specific heat with temperature is greater for HgAzTz than for BaAzTz or PbAzTz.

Explosive properties

Physical properties such as melting point, explosion temperature, percentage of metal ion, colour and bulk density for all the four compounds are shown in Table 6. The friction, impact, and electrostatic charge sensitivities

TABLE 5

Specific heat values

Compound	$C_p (Jg^{-1})$ at		
	370 K	390 K	410 K
$BaAzTz \cdot H_2O$		1.0012	1.15321
PbAzTz	1.1832	1.3052	1.49321
HgAzTz	0.98415	1.3151	1.5841

TABLE 6

Physical properties

Compound	Formula	Formula weight	% Metal	Explosion temperature [a] (°C)	Colour	Bulk density (g cm^{-3})
$Na_2AzTz \cdot H_2O$	$C_2H_2Na_2N_{10}O$	228.00	Calcd. 20.17 Obs.	265	Golden yellow needles	0.92
$BaAzTz \cdot H_2O$	$C_2H_2BaN_{10}O$	319.34	Calcd. 43.00 Obs. 39.98	180	Orange yellow needles	0.81
PbAzTz	C_2PbN_{10}	371.19	Calcd. 55.81 Obs. 51.01	180	Yellow powder	0.88
HgAzTz	C_2HgN_{10}	364.59	Calcd. 54.96 Obs. 51.87	144	Brown lumps	

[a] Explosion temperatures have been determined by heating in DSC at the rate of 10°C min^{-1}.

TABLE 7

Sensitivity results [a]

Compound	Impact sensitivity [b] (height in cm)		Friction sensitivity [c] ft sec^{-1}		Electrostatic charge sensitivity [d] Min. energy reqd. for initiation(J)
	NFL	W_{50}	NFL	W_{50}	
$Na_2AzTz \cdot H_2O$	Not sensitive		Not sensitive		Not sensitive
$BaAzTz \cdot H_2O$	Not sensitive		Not sensitive		Not sensitive
PbAzTz	5.0	7.0	2.0	3.0	0.0303
DPbAzTz	8.0	9.5	2.5	3.25	0.058
CPbAzTz	7.0	8.5	2.5	3.5	0.0428
HgAzTz	4.0	6.5	1.5	2.0	2.2×10^{-6}
DLA	12.0	13.5	4.0	4.5	0.1575
LS	5.0	6.0	7.0	8.0	9.0×10^{-6}

[a] NFL = No fire level; W_{50} = 50% probability; DPbAzTz = dextrinated lead azotetrazole; CPbAzTz = CMC lead azotetrazole; DLA = dextrinated lead azide; LS = lead styphnate.

[b] Ball weight is 28 g.

[c] Weight used is 4 kg.

[d] Gap between the needle and vial is 2 mm.

were measured and the results are summarised in Table 7. Sodium and barium salts were not sensitive to friction and impact under the conditions generally used for primary explosives, whereas, PbAzTz and HgAzTz were highly sensitive to friction and impact. HgAzTz was more sensitive to electrostatic charge than lead styphnate. The compound PbAzTz coated with dextrin showed reduced sensitivity to friction and impact. Not much difference was seen in their sensitivity to electrostatic charge.

After studying their thermal and sensitivity properties, the compounds were tested for their power, i.e. minimum quantity of explosive required to

TABLE 8

Minimum value evaluation using the LPT test

Compound	Minimum quantity [a] (cg)
$Na_2AzTz \cdot H_2O$	35(F), 30(P), 25(P), 20(N)
$BaAzTz \cdot H_2O$	35(F), 30(F), 25(P), 20(N)
PbAzTz	30(F), 25(F), 20(F), 15(P), 10(P), 8(N)
HgAzTz	Not done due to press fire problem
ASA(80:20)	15(F), 10(F), 8(F), 6(F), 5(P), 4(N)

[a] F = Full initiation; P = partial initiation; N = no initiation; LPT = lead plate performance test.

initiate the fixed quantity of base charge of a secondary explosive, e.g. PETN (30 cg). For this study, no. 6 detonators were used and the results were compared with a standard initiator, ASA composition 80 : 20. The results are summarised in Table 8. It is evident that the lead salts are more powerful than other salts. HgAzTz was not tried because of press fire problem. After comparing the efficiency, PbAzTz was tested for its flame sensitivity. Twenty ordinary detonators (no. 6) were fired with 20 cg of PbAzTz. No misfire was noticed. Therefore, it is concluded that PbAzTz is as sensitive as lead azide to friction and impact but more sensitive to flash or spark. However, the power of this salt is less than that of lead azide.

Correlation between the thermal and explosive properties

The thermal and explosive properties of salts of azotetrazoles compare well. The thermal sensitivity increases in the order $Na_2AzTz < BaAzTz < PbAzTz < HgAzTz$. The sensitivity to friction and impact increases in the same order.

CONCLUSIONS

(1) Both the thermal and explosive sensitivities give some indication of the nature of the explosive and safety in handling.

(2) PbAzTz is a powerful salt of azotetrazole and can be used as an initiator, alone, in some special cases, or by mixing with some other initiator. The flame sensitivity is higher than that of lead azide and, therefore, the flame sensitivity of lead azide can be improved by mixing with PbAzTz.

(3) The mercury salt precipitates as a gel and on drying it forms lumps. It is extremely sensitive to friction and therefore should be handled carefully.

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