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A STUDY ON THERMAL AND EXPLOSIVE PROPERTIES OF HYDRAZOTETRAZOLES

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Summary

This paper discusses the results of the thermal decomposition studies on 5,5 -hydrazotetrazole (5,5 HzTz) and its barium, lead and mercury salts Dynamic differential scanning calorimetric and thermogravimetric techniques have been employed in this work Decomposition temperature, heat of decomposition and Arrhenius rate parameters are reported The decomposition data indicate that among the hydrazotetrazoles studied, Pb—HzTz is the least stable compound Explosive properties such as impact, friction and electrostatic sensitivities as well as the initiating power of these compounds have been evaluated These studies show that the lead compound is the most powerful primary explosive among the four compounds investigated It appears that a correlation exists between the thermal decomposition data and the explosive characteristics of the above hydrazotetrazoles

Introduction

In our search for new primary explosives, we previously investigated the thermal decomposition characteristics and explosive properties of several metal azotetrazoles [1] One of the conclusions was that a good correlation exists between the decomposition behaviour and the explosive sensitivity of these compounds In the present study, we have extended this work to hydrazotetrazole and its metal salts The compounds selected include

5,5′-hydrazotetrazole (5,5′-HzTz)
Barium(II) salt of HzTz (Ba—HzTz)
Lead(II) salt of HzTz (Pb—HzTz)
Mercury(II) salt of HzTz (Hg—HzTz)

5,5′-Hydrazotetrazole has been reported by Thiele [2] This compound was investigated for use in primary compositions Mention is also made of Hg—HzTz in the literature [3], although it has not been studied in detail The primary objective of this work is to carry out a systematic study of the thermal decomposition and explosive behaviour of the above hydrazotetrazoles and to seek a correlation between these properties It is hoped

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that the existence of such a correlation in a wide range of compounds would provide a quick and reliable method of screening new materials for potential applications as primary explosives in detonators

Experimental

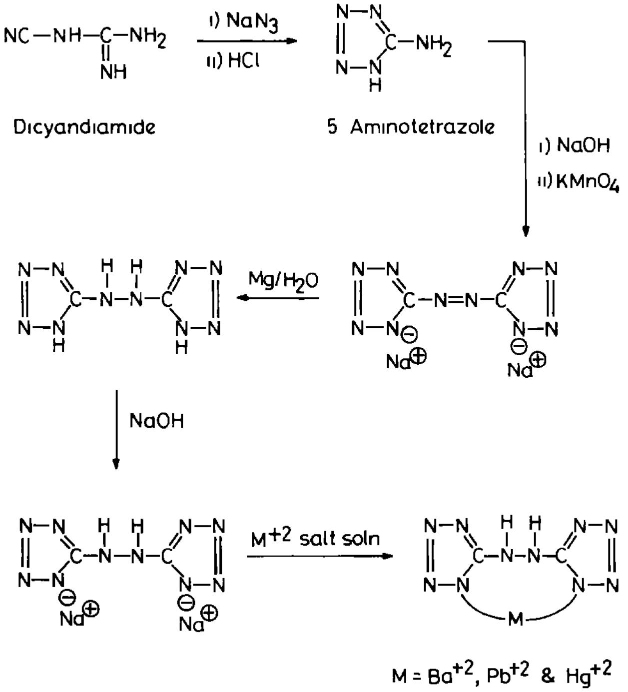
Materials

Preparation of 5,5′-hydrazotetrazole [4]

An amount of 23 g sodium azotetrazole (Na_2^{-}-AzTz) was mixed with 100 ml of distilled water and 50 g of magnesium powder and subjected to gentle reflux for about 3 hours A reaction occurred, at the end of which the yellow solution became almost colourless or sometimes pale yellow Excess magnesium was removed by filtering the hot solution The filtrate was treated with 50 ml 50% HCl to precipitate 5,5′-hydrazotetrazole as a white crystalline material The dried material weighed 15 g (89% yield) and decomposed at 518 K when heated in a glass capillary tube in an electrically heated melting point apparatus

Salts of 5,5′-hydrazotetrazole

5,5′-Hydrazotetrazole was neutralised to pH 7 with 10% NaOH solution Its concentration was adjusted to 0 1 *M* and the solution taken into a stain-



Scheme 1 Preparation of 5,5 -hydrazotetrazole

less steel beaker and heated to 333 K on a water bath A 0 1 *M* solution of an M^{2+} salt (barium, lead or mercury) was placed in a dropping funnel and added dropwise over a period of 10—15 min under stirring The contents of the beaker were further stirred for a period of 15 min at the same temperature After cooling to room temperature, they were filtered and washed first with water and then with ethanol (95%) The resulting HzTz salts dried at room temperature for 3 to 4 hours and then in an air oven at 343 K for 1 hour Yields varied from 70 to 90% in different experiments In the case of the barium salt, the yield was particularly low and not consistent, this may be due to its moderate solubility in water

The preparation of 5,5'-hydrazotetrazole and its metallic salts is shown in Scheme 1 and their physical characteristics are given in Table 1

TABLE 1

Physical characteristics of 5,5 hydrazotetrazole and its metallic salts

Compound	Colour and physical state	Bulk density (g cm^{-3})
5,5 HzTz	White amorphous powder	1 01
Ba—HzTz · H,O	Pale yellow needles	1 10
Pb—HzTz	Yellow amorphous powder	1 05
Hg—HzTz	Brown amorphous powder	0 75

Analysis of composition

CHN analysis This analysis of 5,5'-HzTz was carried out using an automatic analyser (Hewlett—Packard 185 B) For 5,5'-HzTz ($C_2H_4N_{10}$), the results were % calc carbon 14 28, hydrogen 2 38, nitrogen 83 33, % obs carbon 14 01, hydrogen 1 99, nitrogen 83 01 The percentage metal content in the salts was estimated using standard methods [5] The procedures are given below

Lead About 0 2 g of the lead salt was weighed into a 250 ml conical flask, treated with dilute nitric acid, heated, and boiled for a few minutes It was then cooled to room temperature and diluted with distilled water After adding one gram of sodium potassium tartrate, a known excess of 0 05 *M* EDTA was added The pH of the solution was adjusted to 6 using ammonia buffer The excess EDTA was then back-titrated with 0 05 *M* zinc chloride solution using Erichrome Black T as indicator The end point was noted when the solution changed from green to wine-colour Result % lead calc 55 41, obs 52 31 (1 ml of 0 05 *M* EDTA ≡ 10 3695 mg of lead)

Barium About 0 2 g of the barium salt was weighed into a 250 ml conical flask, digested with dilute HCl, cooled to room temperature and diluted with distilled water Analar grade dilute sulphuric acid was run into this flask to precipitate barium as barium sulphate It was filtered through a sintered crucible, washed with water till free from acid and finally with alcohol The crucible was dried at 373 383 K to a constant weight and weighed as $BaSO_4$. Result % barium calc 42 74, obs 39 82

Mercury Mercury salt (about 0 2 g) was digested with dilute HCl and diluted with distilled water The solution was then saturated with H_2S gas and the black precipitate thus formed was filtered through a sintered glass crucible and washed with water, alcohol and carbon disulphide It was then dried at 373—383 K to a constant weight and weighed as HgS Result % mercury calc 54 71, obs 51 87

Thermal analysis

Instruments

Mettler TA-2000C and Perkin—Elmer DSC-1B instruments were used for carrying out the decomposition work The former is able to record both thermogravimetry (TG) and differential scanning calorimetry (DSC) simultaneously Alumina (Al_2O_3) was added as a diluent to prevent explosions during analysis

Procedure

Both TG and DSC thermograms were recorded under non-isothermal conditions with a steady flow rate of He/N_2 of 60 ml/min Various scanning rates, i e , 4, 8, 12, 16, 20 and 25°C min^{-1}, were employed All the runs were recorded after standardising the equipment with prescribed standards Indium and tin (99 9%) metals were used for DSC and $CuSO_4 \cdot 5H_2O$ for TG Samples were weighed in aluminium oxide cups (Alox crucibles and covers with 0 08 ml capacity, ME-24124) and lids with a hole were placed on the cups for the runs in the Mettler instrument, while aluminium cups with uncrimped lids were used for the Perkin—Elmer DSC-1B The sample size was typically in the range of 0.1 to 0 4 mg

Evolved gas analysis for 5,5′-HzTz was carried out on an Associated Electrical Industries (AEI MS-10) mass spectrometer

Explosive properties

Explosive sensitivity to impact, friction and electrostatic charge was measured employing standard methods The impact tests were carried out by the ball drop method, the friction tests using a friction pendulum apparatus [6, 7] and the electrostatic charge test by equipment fabricated in our laboratory, essentially based on the principle of the variable gap technique [8] The minimum value required for the initiation of base charge (PETN) was determined by the lead plate perforation test (LPT)

Results and discussion

Thermal decomposition

Typical thermograms from TG and DSC studies are shown in Fig 1 In the case of Ba—HzTz, the first endotherm in the DSC curve is due to the loss of water of crystallisation The weight loss observed in TG at this stage

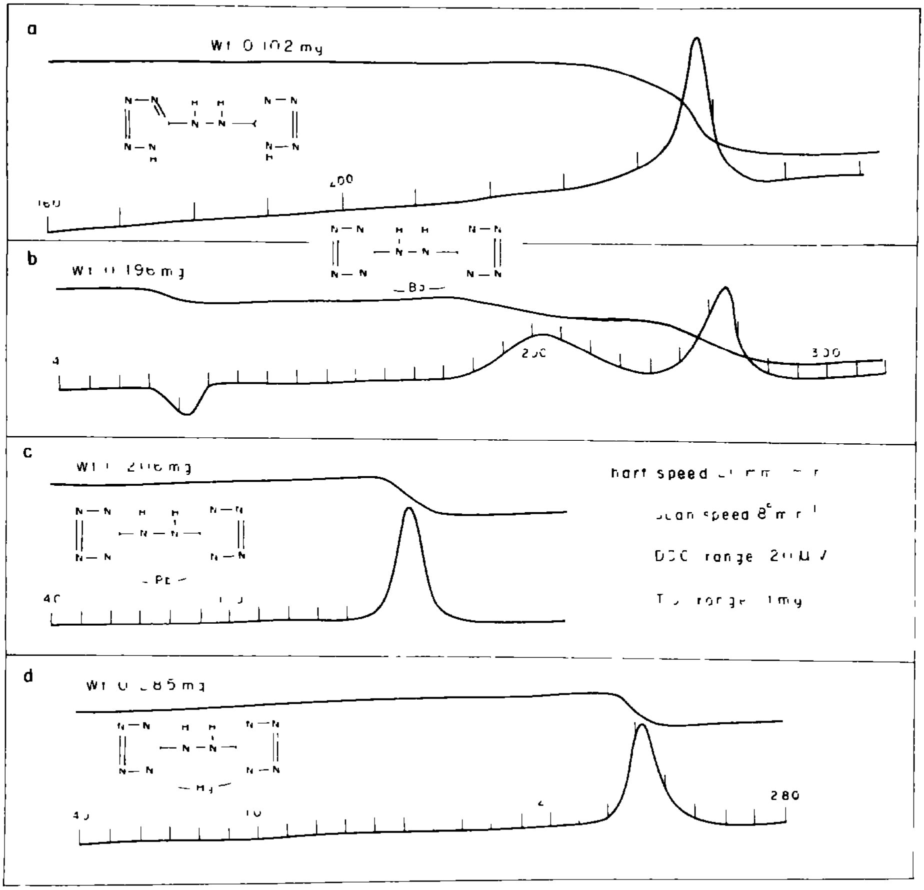


Fig 1 Typical non-isothermal TG—DSC curves of (a) 5,5 hydrazotetrazole, (b) barium—5,5 -hydrazotetrazole, (c) lead—5,5 hydrazotetrazole and (d) mercury—5,5 hydrazotetrazole

is about 5 2%, which is close to the expected weight loss of 5 6% (for the loss of one water molecule) The temperature range for dehydration is 323—343 K This range is slightly less than that of barium azotetrazole (353—373 K) [1] In fact, even the heat of dehydration values show a similar trend. The values are 320.8 and 397 5 J g^{-1} for Ba—HzTz and barium azotetrazole, respectively This indicates that the water molecule is less strongly bound to the former compound

The peak decomposition temperatures, measured in the DSC instrument at a heating rate of 10°C min^{-1}, are given in Table 2 Based on these temperatures, the order of thermal stability is found to be

Pb -HzTz < Hg—HzTz < HzTz < Ba—HzTz

Except for the barium compound, all hydrazotetrazoles studied decompose

TABLE 2

Decomposition data from DSC runs

Compound	Peak decomposition temperature (K)	Heat of decomposition ($kJ\ kg^{-1}$)
5,5 -HzTz	521[a]	2089 2 ± 59 5
Ba—HzTz · H_2O	538[b]	1120 1 ± 39 7[c]
Pb—HzTz	433	1223 5 ± 34 8
Hg—HzTz	505	1210 6 ± 34 1

[a] Heating rate 8°C/min

[b] For exotherm II

[c] Total of exotherms I and II

yielding a single exotherm The peak decomposition temperature listed for Ba HzTz refers to the second exotherm Table 2 also lists the heat of decomposition values for all the four compounds The ΔH_{decomp} values for the three metal derivatives are close to each other, while that for the parent HzTz is almost twice as large Table 3 lists the percentage weight loss observed in TG runs

TABLE 3

Observed percentage weight loss in TG

Compound	Dehydration (%)	Decomposition (%)
5,5 HzTz	—	78 00—79 00[a]
Ba—HzTz · H_2O	5 2	20 00—23 00
Pb—HzTz	—	17 50—19 50
Hg—HzTz	—	18 50—21 00

[a] The values are average values for five runs For decomposition, the weight loss increased with increased heating rate

The kinetics of dehydration of Ba -HzTz · H_2O and that of decomposition for all the four compounds have been evaluated from the TG and DSC curves recorded under non-isothermal conditions using standard methods Thus, the activation energy for dehydration has been obtained using the methods of Rogers and Morris [9], Borchardt and Daniels [10] and Coats and Redfern [11]

Rogers and Morris [9] assume that the rate constant at a given temperature is proportional to the height of the peak Therefore, the activation energy, E_{act}, is obtained from the slope of a straight-line plot of log b (where b is the height of the peak) against $1/T$ The value of E_{act} for the dehydration of Ba—HzTz · H_2O thus obtained is 329 6 ± 8.2 kJ mol^{-1}

Borchardt and Daniels [10] have suggested that E_{act} could be calculated using the equation

$$\ln \frac{b}{(1 - \alpha)^n} = \ln CA - \frac{E_{act}}{RT} \qquad (1)$$

where b is the deflection from the base line, α is the ratio of the area of the exotherm up to b to the total area of the exotherm, n is the order of the reaction, C is a constant, A is the frequency factor and R is the gas constant It has been found for the dehydration curve that when $n = 1$, a perfect straight line is obtained with a correlation coefficient of 0 98 Therefore, the dehydration follows a first-order mechanism The value of E_{act} is 342 5 ± 10 1 kJ mol^{-1}

In the third method [11], E_{act} is obtained from the equation

$$\log \left[1 \quad \frac{(1 - \alpha)}{T^2(1 - n)}\right]^{1-n} = \log \frac{AR}{aE_{act}} \left[1 - \frac{2RT}{E_{act}}\right] - \frac{E_{act}}{2\ 3RT} \qquad (2)$$

The best fit has been found for $n = 1$ and $E_{act} = 328\ 0 \pm 9\ 2$ kJ mol^{-1}

The kinetics of decomposition of the four hydrazotetrazoles were also investigated by several methods The α- -t and α—reduced time curves have been plotted for all four compounds The former were of sigmoid type while the latter indicated that the same mechanism of decomposition is valid at different heating rates Typical curves for 5,5'-HzTz (from DSC experiments) are shown in Figs 2 and 3 The Arrhenius parameters have been computed using the three methods mentioned earlier in addition to the Ozawa [12] and Kissinger [13] methods The last two are based on the

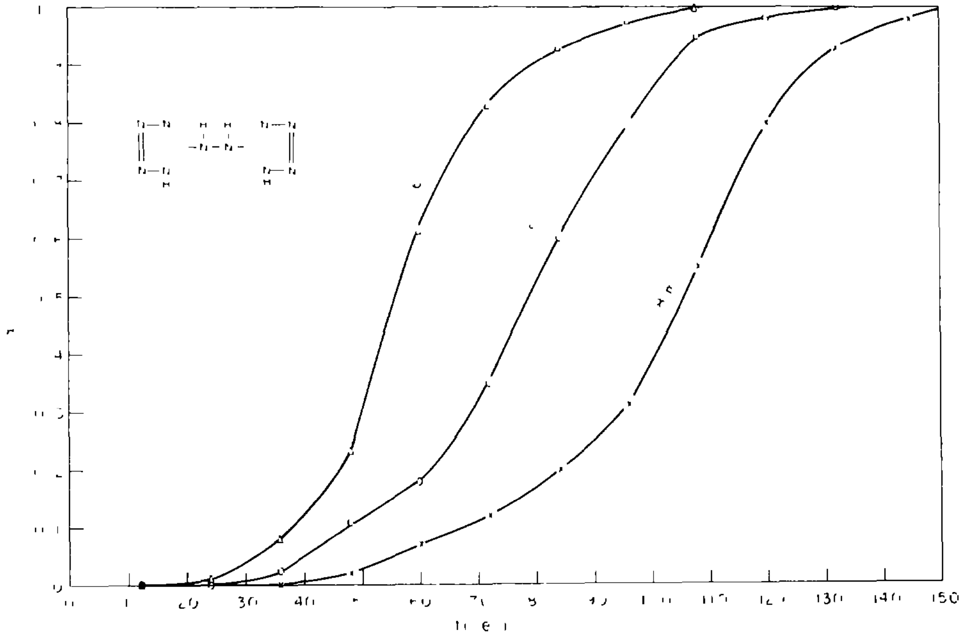


Fig 2 Typical α—time plots for 5,5 -hydrazotetrazole decomposition in dynamic runs

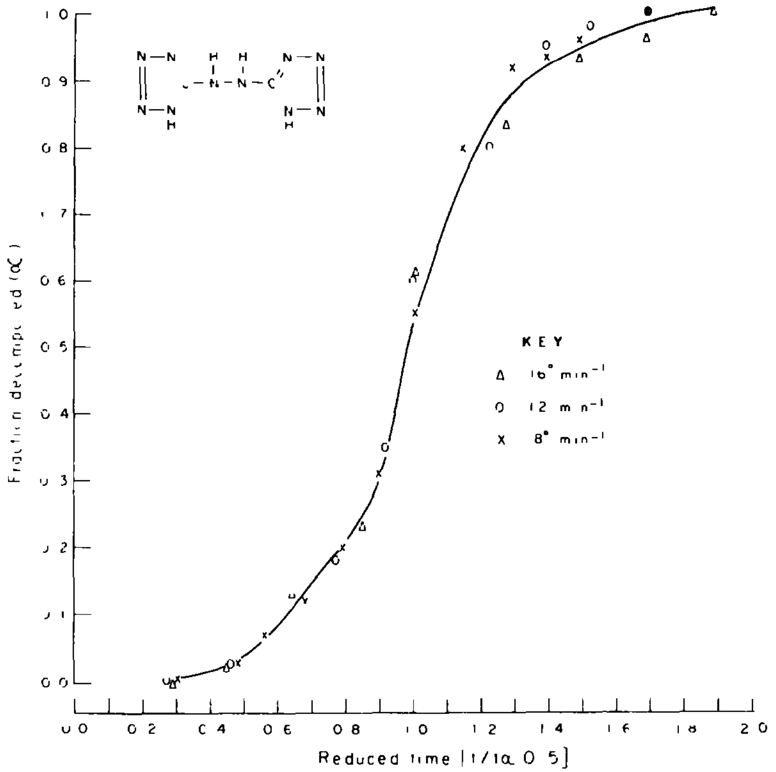


Fig 3 Typical α—reduced time plots for decomposition of 5,5 -hydrazotetrazole in dynamic runs

shift in peak temperature with the heating rate Typical plots obtained using the various methods are shown in Figs 4—6, while the E_{act} values are given in Table 4

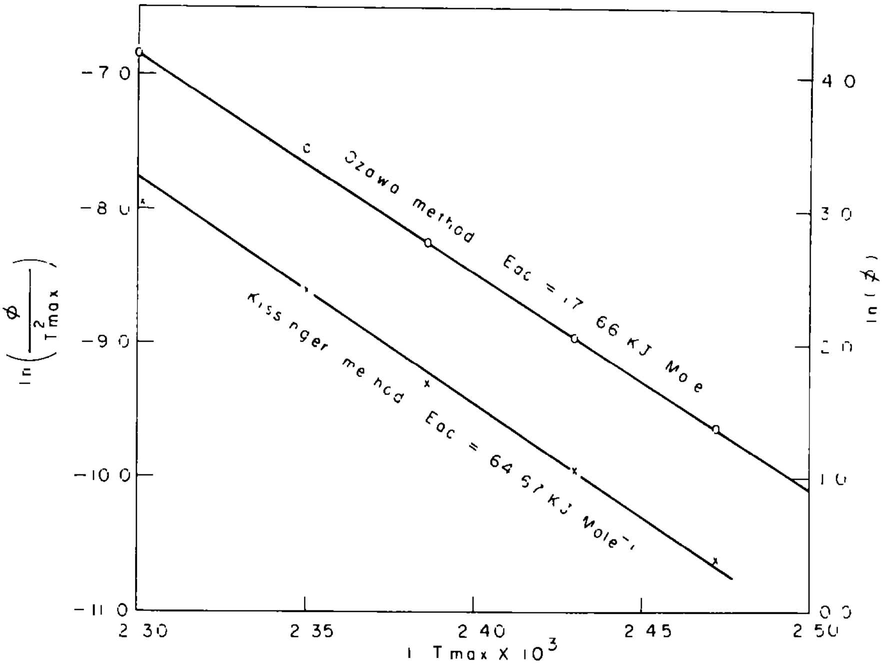
The results obtained by all these methods indicate that the decomposition is not following a simple order of reaction Doulah [14] developed a method to determine the mechanism of decomposition It is essentially based on the Avrami—Erofeeyev equation, and it can be employed for both TG and DSC techniques For this method, the estimation of α values at different temperatures and inception temperatures are required A plot of ln ln[1/(1 − α)] against ln($T - T_0$) gives a straight line with a slope of β This method utilises the equation given below

$$\ln \ln[1/(1 - \alpha)] = \beta \ln t + b \ln \gamma \qquad (3)$$

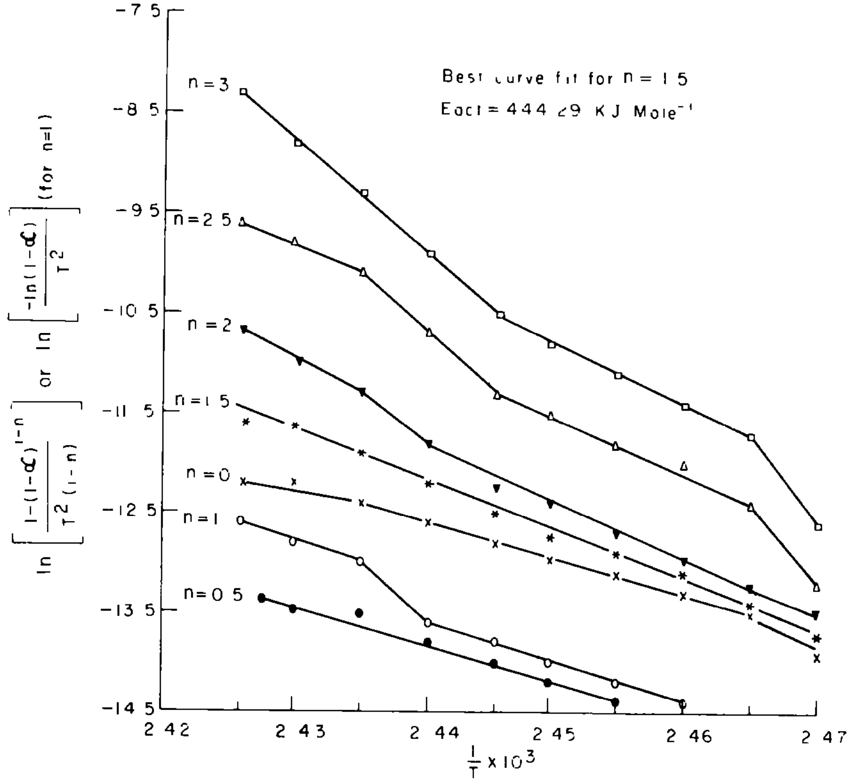
where $t = (T - T_0)/\phi$ for dynamic runs, φ is the heating rate, T is the temperature at a given α, T_0 is the inception temperature When β = 1, the de-

Fig 4 Oazwa and Kissinger methods for lead—5,5 hydrazotetrazole

Fig 5 Typical Coats and Redfern plots for TG-analysis of non isothermal decomposition of lead—5,5 -hydrazotetrazole at various values of order of reaction



-7 0
-8 0
-9 0
-10 0
-11 0
$\ln\left(\frac{\phi}{T^2_{max}}\right)$
4 0
3 0
2 0
1 0
0 0
ln (φ)
2 30
2 35
2 40
2 45
2 50
1 Tmax X 10^3
Ozawa method Eac = 17 66 KJ Mole
Kissinger method Eac = 64 57 KJ Mole^{-1}



Best curve fit for n = 1 5
Eact = 444 29 KJ Mole^{-1}
$\ln\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ or $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$ (for n=1)
-7 5
-8 5
-9 5
-10 5
-11 5
-12 5
-13 5
-14 5
n = 3
n = 2 5
n = 2
n = 1 5
n = 0
n = 1
n = 0 5
2 42
2 43
2 44
2 45
2 46
2 47
$\frac{1}{T}$ x 10^3

composition follows first-order kinetics, when $1 < \beta \leqslant 3$, 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 value for β obtained for the hydrazotetrazoles under study is around 2 5 Therefore, the decomposition occurs at the phase boundary of the products

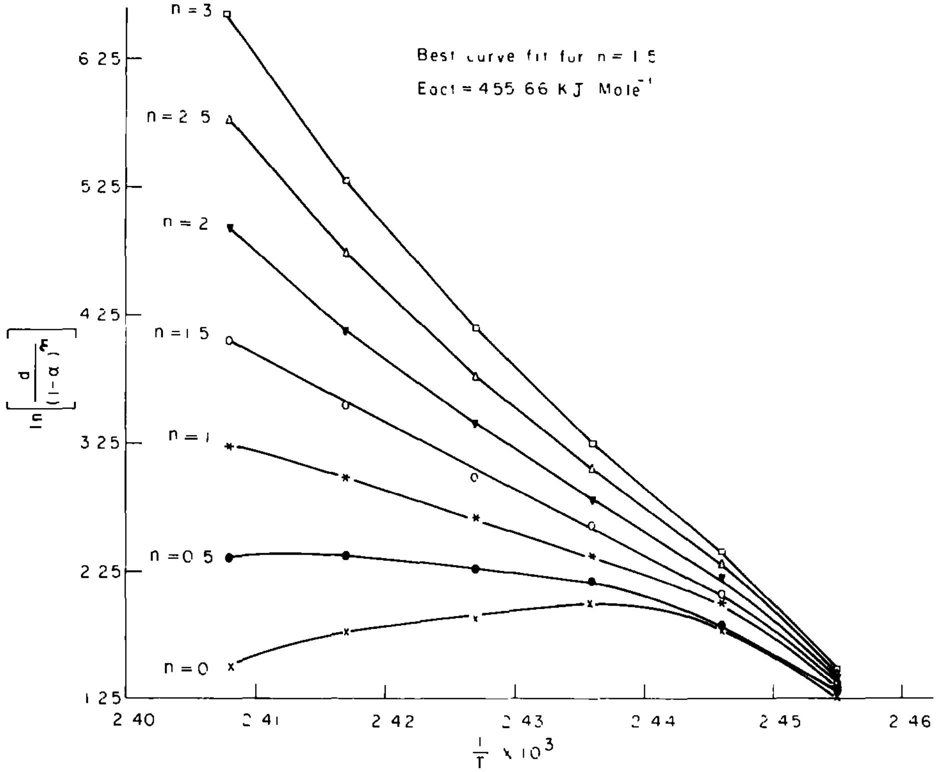


Fig 6 Typical Borchardt and Daniels plots for various values of order of reaction for the decomposition of lead—5,5 -hydrazotetrazole

TABLE 4A

Decomposition kinetics parameters from DSC experiments (E_{act} in kJ mol^{-1})

Compound	Method				
	Ozawa	Kissinger	Rogers and Morris	Borchardt and Daniels	Coats and Redfern
5,5 -HzTz	605 50	601 50	727 50	305 00 (n = 2)	302 80
Ba—HzTz • H_2O	223 50	216 75	713 00	704 00 (n = 1 5)	706 80 (n = 1 5)
Pb—HzTz	171 50	164 50	428 00	423 50 (n = 1 5)	411 00 (n = 1 5)
Hg—HzTz	268 00	285 00	390 55	385 50 (n = 1 5)	396 60 (n = 2)

Note the value assigned to n is the one which gave the best curve fit with a 0 98 index of correlation

TABLE 4B

Decomposition kinetics parameters from TG experiments (E_{act} in kJ mol^{-1})

Compound	Method of Coats and Redfern
5,5 -HzTz	785 80 (n = 1 5)
Ba—HzTz · H_2O	726 50 (n = 1 5)
Pb—HzTz	444 00 (n = 1 5)
Hg—HzTz	412 50 (n = 2)

Note the value assigned to n is the one which gave the best curve fit with a 0 98 index of correlation

Explosive properties

Results from impact, friction and electrostatic charge sensitivity tests are presented in Table 5 In general, it could be stated that, except for electrostatic sensitivity, the lead compound is the most sensitive, while the barium and mercury derivatives are the least sensitive The data from electrostatic sensitivity tests show an entirely different trend, with Hg—HzTz as the most sensitive compound We had observed a similar pattern in the sensitivity data for mercury - and lead--azotetrazoles [1] Although the impact and friction sensitivities of these two compounds were comparable, the minimum energy required for initiation in the electrostatic sensitivity test was 2 2 × 10^{-6} J for the former compound, compared to 0 0303 J for the latter Thus, it appears that the parameters which determine the sensitivity of an explosive to impact and friction are different from those which govern its sensitivity to electrostatic charge Excluding the data from the

TABLE 5

Sensitivity results

Compound	Impact sensitivity[a]		Friction sensitivity[b]		Electrostatic sensitivity[c] (Energy required for initiation (J))
	NFL (cm)	W_{50} (cm)	NFL ($m\ s^{-1}$)	W_{50} ($m\ s^{-1}$)	
5,5 -HzTz	0 0	12 5	2 9	3 2	ns
Ba—HzTz · H_2O	ns	ns	ns	ns	ns
Pb—HzTz	10 0	12 5	0 6	0 8	1 518 × 10^{-2}
Hg—HzTz	ns	ns	3 0	3 2	6 2 × 10^{-6}
DLA	12 0	13 5	1 2	1 4	1 575 × 10^{-1}
LS	5 0	6 0	2 1	2 4	9 0 × 10^{-6}

NFL No fire level
W_{50} 50% probability level
ns not sensitive
[a] Ball weight is 28 g
[b] Load weight is 4 kg
[c] Gap between the needle and vial is 2 cm

third test, the four hydrazotetrazoles could be ordered as follows with regard to their sensitivity

Pb—HzTz > HzTz > Hg—HzTz > Ba—HzTz

This trend could be explained based on the thermal decomposition characteristics Pb—HzTz possesses the lowest peak decomposition temperature, while the barium compound, being a hydrate, should expend about 0 32 kJ g^{-1} before explosive initiation could occur The higher sensitivity of 5,5'-HzTz compared to Hg—HzTz could be attributed to its much higher heat of decomposition (see Table 2) From the above discussion, it is evident that a correlation could be drawn between the thermal decomposition behaviour and explosive properties of hydrazotetrazoles However, it must be mentioned here that due consideration must also be given to the role of mechanical properties such as hardness, coefficient of friction etc of the explosive crystals influencing the sensitivity characterstics

Incidentally, it could be mentioned here that a commonly observed structure--property correlation for some metallic azides [15], — the greater the ionisation potential of the cation, the more sensitive the compound — does not appear to be valid in the case of hydrazotetrazoles The ionisation potentials of the cations under discussion follow the pattern

$H^+ > Hg^{2+} > Pb^{2+} > Ba^{2+}$

However, as stated earlier, the observed sensitivity trend is different from the above The azotetrazoles, on the contrary, do exhibit the above correlation [1]

Finally, experiments were carried out to investigate the initiating efficiency of the hydrazotetrazoles, i e , the minimum quantity of explosive required to initiate a fixed quantity of base charge of a secondary explosive, e g PETN (pentaerythritol tetranitrate) For this study, No 6 strength detonators were used, the results are listed in Table 6 It is clear that Pb-HzTz possesses the highest initiating efficiency followed by Hg—HzTz, while Ba—HzTz and 5,5'-HzTz have similar efficiency The "minimum value evaluation" data also follow the trend observed in the thermal decomposition studies

TABLE 6

Minimum value evaluation by lead plate test

Compound	Charge weight (cg)
5,5 HzTz	35(F), 30(P), 25(P), 20(N)
Ba—HzTz · H_2O	35(F), 30(F), 25(P), 20(N)
Pb—HzTz	35(F), 30(F), 25(F), 20(F), 15(F), 13(P), 10(N)
Hg—HzTz	35(F), 30(F), 25(P), 20(P), 15(N)
DLA	5(F), 3(N)

F full initiation
P partial initiation
N no initiation

Conclusions

1 Although it is mentioned in the literature that 5,5′-HzTz is "powerful" and can be used as a primary explosive, the present study indicates that it cannot be used alone as an initiatory explosive

2 Pb-HzTz is the most powerful among the hydrazotetrazoles studied and shows promise as a primary explosive

3 A comparison of the thermal decomposition characteristics and the explosive properties reveals that there is a good correlation among them, and therefore DSC offers a quick and reliable method of screening potential explosives

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