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THE THERMAL DECOMPOSITION OF THE SILVER(I) AND MERCURY(II) SALTS OF 5-NITROTETRAZOLE AND OF MERCURY(II) FULMINATE

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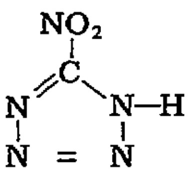
ABSTRACT

Silver and mercury(II) nitrotetrazoles (NT) are possible alternative detonants to lead azide. AgNT is the thermally more stable compound, decomposing between 485 and 525 K, compared with 440—460 K for $Hg(NT)_2$. Decomposition of AgNT is accompanied by melting and leads to a silver metal product, while decomposition of $Hg(NT)_2$ is accompanied by some volatilization of mercury. Similar volatilization was not observed at the lower temperatures (380—400 K) required for the decomposition of mercury(II) fulminate. On a mass basis, the heat evolved during decomposition of the nitrotetrazoles is up to 25% greater than that for the mercury fulminate or lead azide decomposition. Apparent activation energies, which represent the experimental temperature coefficients of these decompositions, are similar (135—165 kJ $mole^{-1}$) except for the earlier stages of the AgNT decomposition (246 kJ $mole^{-1}$).

INTRODUCTION

In 1975, Bates and Jenkins [1], after examination of a large number of possible substances, proposed that the silver and mercury(II) salts of 5-nitrotetrazole (HNT)



might be suitable alternatives, as detonants, for lead(II) azide. Lead azide has the well-known disadvantages of being readily hydrolysed by traces of moisture, leading to possible formation of more hazardous azides (basic lead azide), and of being incompatible with metal and polymeric materials used in fuse design.

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Silver nitrotetrazole, AgNT, has certain disadvantages [1] in that at least six polymorphic forms have been identified and that it dead-presses at low loads (≃20 MPa). Mercury(II) nitrotetrazole, Hg(NT)$_2$, does not exhibit polymorphism and gave a superior performance, mass for mass, to lead azide in the small detonator. Scott [2] has reported on some of the explosive properties of Hg(NT)$_2$. Details of the thermal decomposition of these compounds have not been reported.

Results obtained for the decomposition of Hg(NT)$_2$ (see below) suggested that some aspects of the thermal decomposition of mercury(II) fulminate should be re-examined. Results of such a re-examination are included in this paper.

TABLE 1

X-Ray powder diffraction data for AgNT, Hg(NT)$_2$, Hg(CNO)$_2$ and their decomposition products *

AgNT	Stage I product	Stage II product	Hg(NT)$_2$	Product	Hg(CNO)$_2$	Product (amorphous) faint rings centred on
11.04 (v.s.)	7.75	2.37 (v.s.)	6.23 (w)	3.03 (v.s.)	5.37	~5.0
7.37 (s)	5.40	2.01 (s)	5.60 (s)	2.26	4.07 (s)	
5.33 (w)	5.21 (w)	1.43 (s)	5.40 (s)	2.07	3.95	
4.67 (w)	4.23 (s)	1.22 (v.s.)	4.98	1.90 (s)	3.07	
4.57 (w)	3.50 (s)	1.17	4.15 (s)	1.86 (s)	2.98	
4.43 (w)	3.25		3.64 (w)		2.71 (s)	~2.8
4.23 (w)	2.88		3.14 (s)		2.52 (w)	
4.00 (s)	2.71		2.90 (w)		2.37 (w)	
3.86 (v.s.)	2.66 (w)		2.79		2.25 (s)	
3.61	2.35		2.63 (w)		2.15 (w)	
3.42	2.10		2.56		2.02	
3.30	1.92		2.47 (w)		1.89 (w)	
3.18 (s)			2.40 (w)		1.80 (w)	
2.96 (s)			2.37 (w)		1.74	
2.86			2.34		1.70 (w)	
2.78			2.25 (w)		1.67	
2.63			2.18 (w)		1.57	
2.56			2.13 (w)		1.54 (w)	
2.40			2.08		1.51	
2.25			2.02		1.47	
2.12			2.01		1.45	
2.06			1.97		1.40	
2.00			1.92 (w)		1.37	
1.92 (s)			1.88 (w)			
1.81			1.84 (w)			
1.74			1.79 (w)			
1.62			1.76 (w)			
			1.74			
			1.70			
			1.64			
			1.57			

* (v.s.) indicates very strong line, (s) indicates strong line, (w) indicates faint line.

EXPERIMENTAL

Samples of AgNT, $Hg(NT)_2$ and $Hg(CNO)_2$ were powders as supplied by E.R.D.E., Waltham Abbey. X-Ray powder diffraction photographs of the nitrotetrazoles and their decomposition products were taken using Ni K_α radiation, and the d-values obtained are given in Table 1. Data for $Hg(CNO)_2$ agreed closely with that given in the Powder Data File.

Thermogravimetry on sample masses of less than 1 mg was carried out on a Stanton 750 thermobalance, in 50 ml min^{-1} of argon unless otherwise specified, with output via a DVM to a tape-punch. Tapes were processed on a Hewlett-Packard 9825A calculator and plotter.

Thermochemical measurements were made using a Perkin-Elmer DSC-2 differential scanning calorimeter. Small samples (<0.5 mg) were used to reduce the risk of explosion and contamination of the instrument with volatile mercury compounds. Enthalpy values were estimated by comparison with the enthalpy of melting of known masses of pure indium metal.

RESULTS AND DISCUSSION

Silver nitrotetrazole (AgNT)

The thermal decomposition of AgNT (AgN_4CNO_2) in argon at a programmed temperature increase of 2 K min^{-1} takes place in two stages (Fig. 1). These stages are more readily distinguishable under isothermal conditions where the first stage corresponds to a mass loss of 42 ± 1% and the overall decomposition to 52 ±2% of the original sample mass. Similar stages were observed in an atmosphere of oxygen. The first stage in argon occurs at conveniently measurable rates in the range 485—525 K (210—250°C). The kinetics of the second stage were not studied, but reaction was taken rapidly to completion at 573 K (300°C) to check the overall mass losses.

Decomposition to silver metal as the only solid residue

$$AgN_4CNO_2(s) \rightarrow Ag(s) + \text{gases}$$

would give an expected mass loss of 51.4%, which is in agreement with the overall behaviour observed. Formation of Ag_2O

$$2\,AgN_4CNO_2(s) \rightarrow Ag_2O(s) + \text{gases}$$

corresponds to a mass loss of 47.8%. Any Ag_2O formed under the conditions used is unlikely to be stable [3]. X-Ray diffraction confirmed that the final product was silver metal. A brownish-black intermediate gave the powder data in Table 1, but was not further identified.

The kinetics of the first stage of decomposition of AgNT in argon at a flow rate of 50 ml min^{-1} were determined at a series of constant temperatures in the range 485—526 K (212—253°C). Mass losses with time were converted to fractional decomposition, α, versus time curves as illustrated in Fig. 2. These α—time curves have an initial approximately linear region up to $\alpha \simeq 0.4$ followed by a deceleratory region. Plots on reduced-time scales such

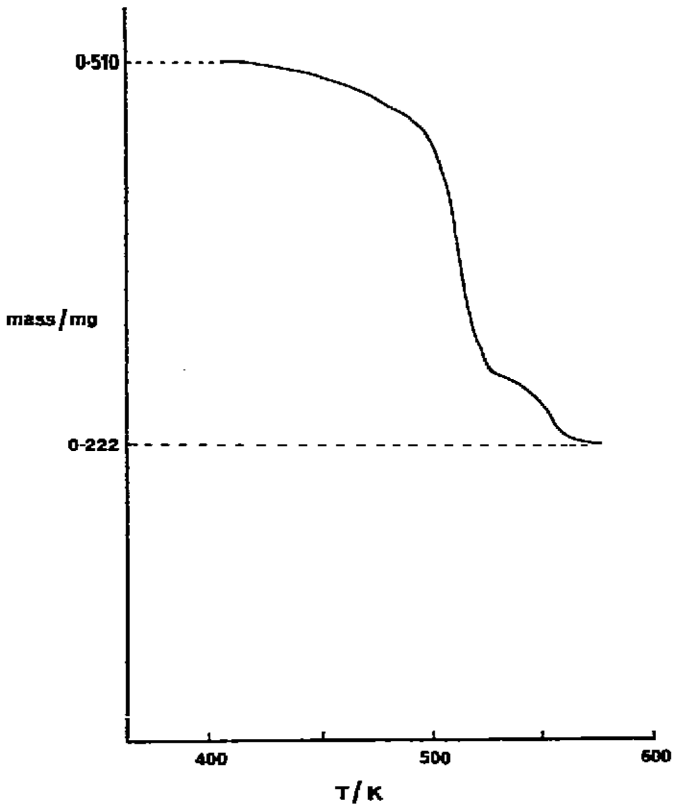


Fig. 1. TG trace for AgNT in argon (50 ml min^{-1}) at 2 K min^{-1}.

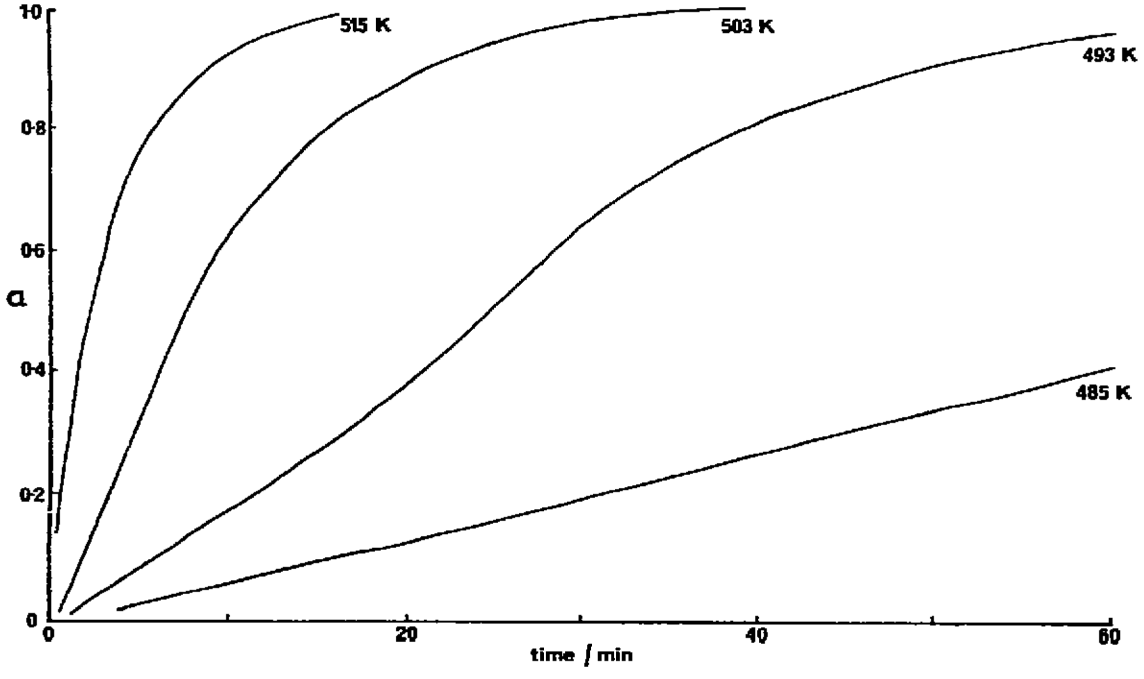


Fig. 2. Isothermal decomposition of AgNT in argon (50 ml min^{-1}).

that $\alpha = 0.5$ at $t_{\mathrm{red}} = 1.0$ (Fig. 3), or $\alpha = 0.7$ at $t'_{\mathrm{red}} = 1.0$ did not give very good coincidence, which suggests a complex mechanism which changes with temperature.

The slopes of the initial linear regions of the α—time curves were used as estimates of the zero-order rate coefficients, k_{I}

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k_{\mathrm{I}} \qquad (0 < \alpha < 0.4)$$

The deceleratory region was analysed in terms of the more common models [4], viz. the unimolecular decay (F1)

$$-\ln(1 - \alpha) = k_{\mathrm{F1}}(t - t_0)$$

the contracting area (R2)

$$1 - (1 - \alpha)^{1/2} = k_{\mathrm{R2}}(t - t_0)$$

and the contracting volume (R3)

$$1 - (1 - \alpha)^{1/3} = k_{\mathrm{R3}}(t - t_0)$$

Plots of these expressions for the decomposition at 503 K are shown in Fig. 4. (Note that F1 has been scaled to 1/5 for comparison.) It is known to be difficult [5] to distinguish clearly which of this group of expressions is most applicable. This is evident from Fig. 4 where F1 is approximately linear over the range $0.3 < \alpha < 0.9$, while R3 applies better for $0.7 < \alpha < 0.98$. The applicability of R2 and R3 was slightly dependent upon temperature,

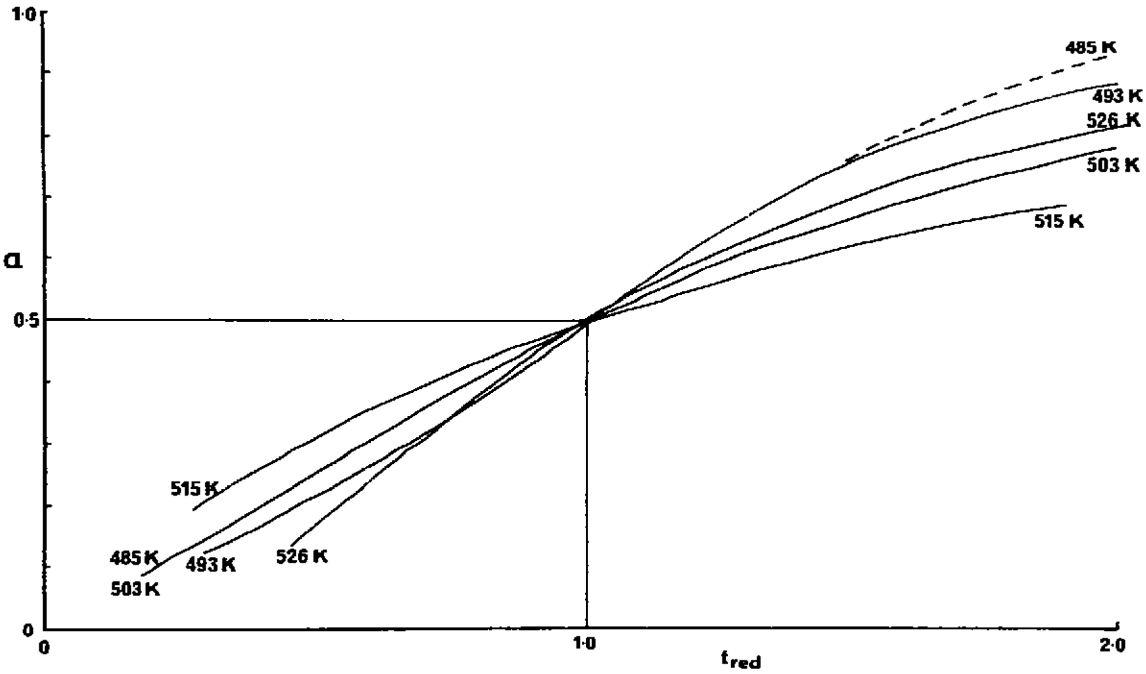


Fig. 3. Reduced-time curves for the isothermal decomposition of AgNT $\alpha = 0.5$ at $t_{\mathrm{red}} = 1.0$.

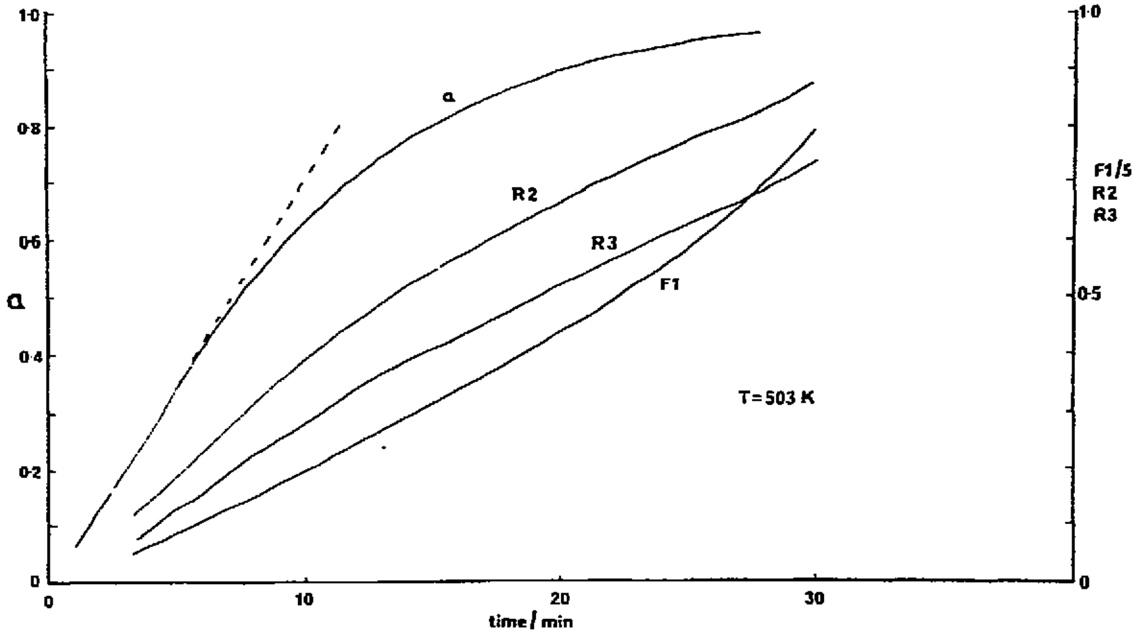


Fig. 4. Trial analyses for the decomposition of AgNT at 503 K.

becoming poorer at the higher end of the temperature range. The fit of F1 was more consistent. Rate coefficients, k_{F1}, k_{R2} and k_{R3}, were estimated from the slopes of the least squares line calculated for the model expressions. Rate coefficients for the decomposition in an oxygen atmosphere were about 30% greater than in argon at the same temperature. From the temperature dependence of the rate coefficients k_{F1}, k_{R2} and k_{R3} and of k_I for the initial region, apparent activation energies, E_a, and frequency factors, A, were calculated. These are given in Table 2.

From Table 2, it is evident, as has been shown before [6], that estimation of apparent Arrhenius parameters is not very dependent upon the model kinetic expression chosen.

TABLE 2

Apparent Arrhenius parameters for the thermal decomposition of AgNT

Stage	Isothermal (485-526 K)			Non-isothermal[7]		
	Analysis	E_a/kJ mole^{-1}	ln(A/min^{-1})	n	E_a/kJ mole^{-1}	ln(A/min^{-1})
I					190 ± 14	48
II	Zero order	246 ± 24	56.3	1	240 ± 12	56
III	F1	166 ± 11	37.8	1	160 ± 16	38
	R2	158 ± 16	34.1			
	R3	160 ± 14	34.5			

A non-isothermal TG run was analysed using the method of Hauser and Field [7] in which an equation of the form

$$\frac{dm}{dt} = -A_i \exp(-E_i/RT)\, m^n$$

is assumed to apply over the whole decomposition range, with m the fractional residual mass ($= 1 - \alpha$) and the subscript i referring to various reaction stages. Plots of $\ln(-dm/dt) - \ln(m^n)$ against $1/T$ are then used to determine the best value of the exponent n and the values of E_i and A_i for the reaction stages. The results obtained using this method are included in Table 2 and show good agreement with those obtained from isothermal studies. The reaction has two main stages and a small (~1½%) mass loss is observed to occur some 20 K before the main decomposition.

The complex nature of the decomposition kinetics is confirmed by the DSC trace (Fig. 5). The enthalpy change for the overall decomposition exotherm was estimated as -430 ± 20 kJ mole^{-1} (-1.94 ± 0.10 kJ g^{-1}). Examination of the initially colourless and transparent, irregularly shaped crystallites on the hot stage of an optical microscope showed that melting accompanies decomposition. The silver product is extensively sintered, rather than completely fused, owing to its high melting point. The occurrence of melting would account for the irregularity of the observed kinetics, with the lower activation energy for the deceleratory region probably referring to decomposition in an, at least, partially molten system.

Mercury(II) nitrotetrazole [$Hg(NT)_2$]

On heating $Hg(NT)_2$ at 2 K min^{-1} in argon, decomposition begins above 435 K (162°C) and is complete by 500 K. The overall mass loss at 500 K is 94% of the original sample mass. The little solid residue is an orange-red powder, pseudomorphic with the reactant crystallites but largely amorphous to X-rays. On extended exposure, a small proportion of crystalline material was detectable (see Table 1).

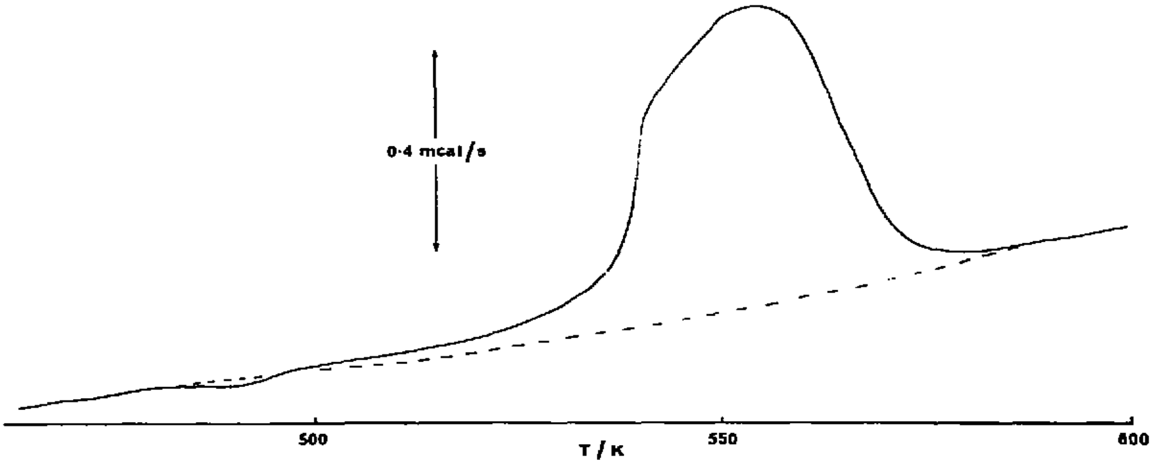


Fig. 5. DSC trace for AgNT (0.45 mg) in nitrogen at 5 K min^{-1}.

Under isothermal conditions, decomposition occurs at conveniently measurable rates over the temperature range 438—461 K (165—188° C). The average overall mass loss under these conditions was 86 ±1% which indicates that mercury, or a volatile compound of mercury, is one of the decomposition products [Hg in $Hg(NT)_2$ is 47.5% by mass]. Mass losses with time were converted to fractional decomposition (α) versus time curves as illustrated in Fig. 6. Sigmoid curves like these usually conform to either the Avrami—Erofeev equation [4]

$$\{-\ln(1-\alpha)\}^{1/n} = k_n(t-t_0)$$

with an appropriate value of n (model An), or to the Prout—Tompkins equation (model B1):

$$\ln\{\alpha/(1-\alpha)\} = k_B(t-t_0)$$

The Prout—Tompkins expression did not represent the experimental results satisfactorily, while the best value of n for use in the Avrami—Erofeev equation is not always clearly distinguishable [5]. Trial analyses for $n = 2$, 3 and 4 are illustrated in Fig. 7 for the decomposition at 450 K ($0.05 < \alpha < 0.95$). There is some curvature in each of the plots, but $n = 2$ appears to fit best over the deceleratory period. Comparison of the fit over the two ranges $0.05 < \alpha < 0.5$ and $0.5 < \alpha < 0.95$ gave the rate coefficients listed in Table 3 and confirmed that $n = 2$ applies best over the deceleratory period, but either $n = 3$ or $n = 4$ could apply to the acceleratory period.

In an attempt to distinguish between these possibilities more clearly, all the experimental α—time curves were converted to reduced-time scales ($t_{red} = t/t_{0.5}$), where $t_{0.5}$ is the time at each temperature at which $\alpha = 0.5$ These plots all lie on a single curve (see Fig. 8) suggesting that a single

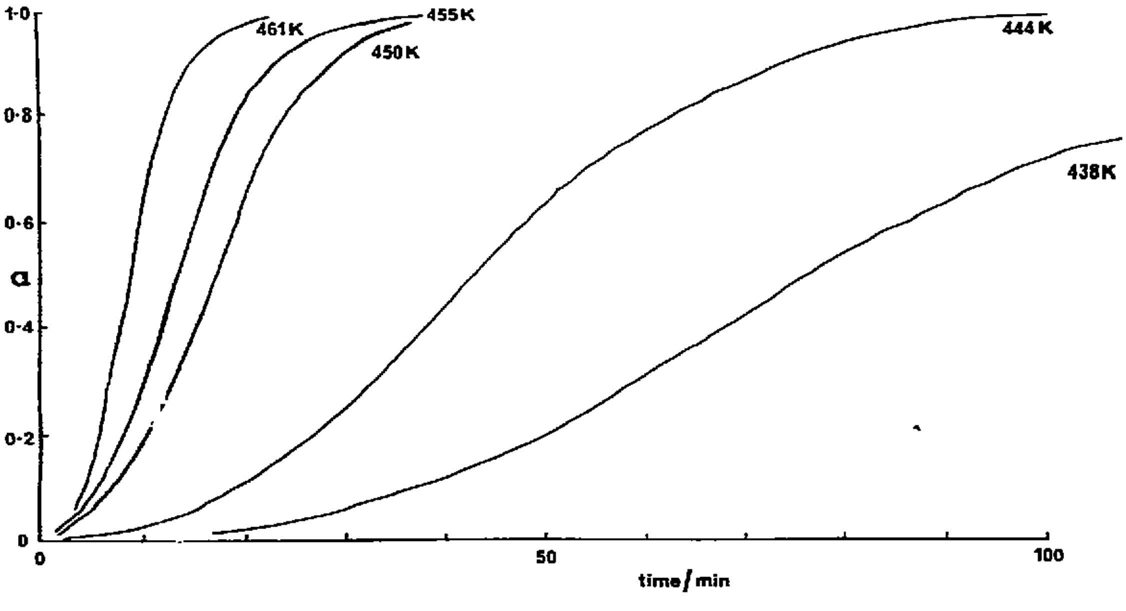


Fig. 6. Isothermal decomposition of $Hg(NT)_2$ in argon (50 ml min^{-1}).

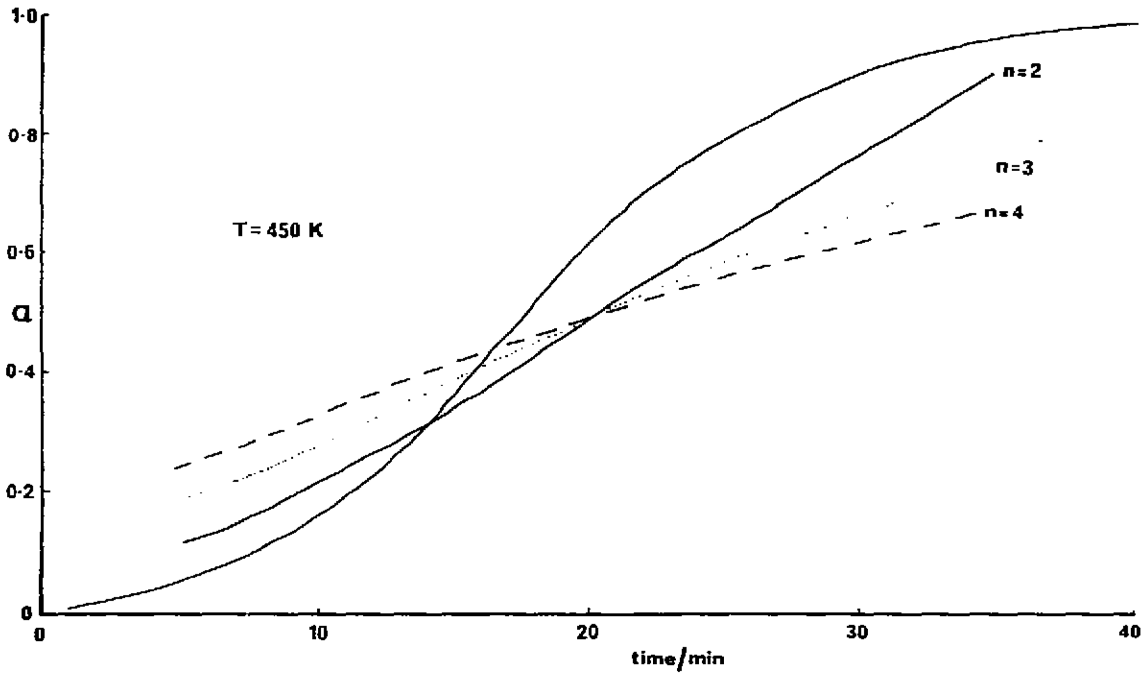


Fig. 7. Trial analyses, in terms of the Avrami—Erofeev model, for the decomposition of $Hg(NT)_2$ at 450 K.

decomposition mechanism applies throughout the temperature range 438—461 K. Comparison of this composite experimental curve with the theoretical reduced-time curves for the Avrami—Erofeev model

$$\alpha = 1 - \exp\{-(k_{0.5}t_{red})^n\}$$

where $k_{0.5} = \{-\ln(0.5)\}^{1/n}$, see Fig. 8, confirms that the deceleratory period conforms most closely to $n = 2$, while the acceleratory period is fitted best when n lies between 2 and 3, rather than between 3 and 4 as suggested

TABLE 3

Applicability of the Avrami—Erofeev model to the decomposition of $Hg(NT)_2$ at 450 K in Ar

	$n = 2$	$n = 3$	$n = 4$
k for $0.05 < \alpha < 0.95$	0.0546	0.0379	0.0293
Standard error in k	0.0001	0.0001	0.0002
Correlation coefficient	0.9993	0.9983	0.9953
k for $0.05 < \alpha < 0.5$	0.0481	0.04095	0.03484
Standard error in k	0.0003	0.00008	0.00007
Correlation coefficient	0.9977	0.9997	0.9997
k for $0.5 < \alpha < 0.95$	0.0553	0.0338	0.0243
Standard error in k	0.0001	0.0001	0.0001
Correlation coefficient	0.9997	0.9992	0.9985

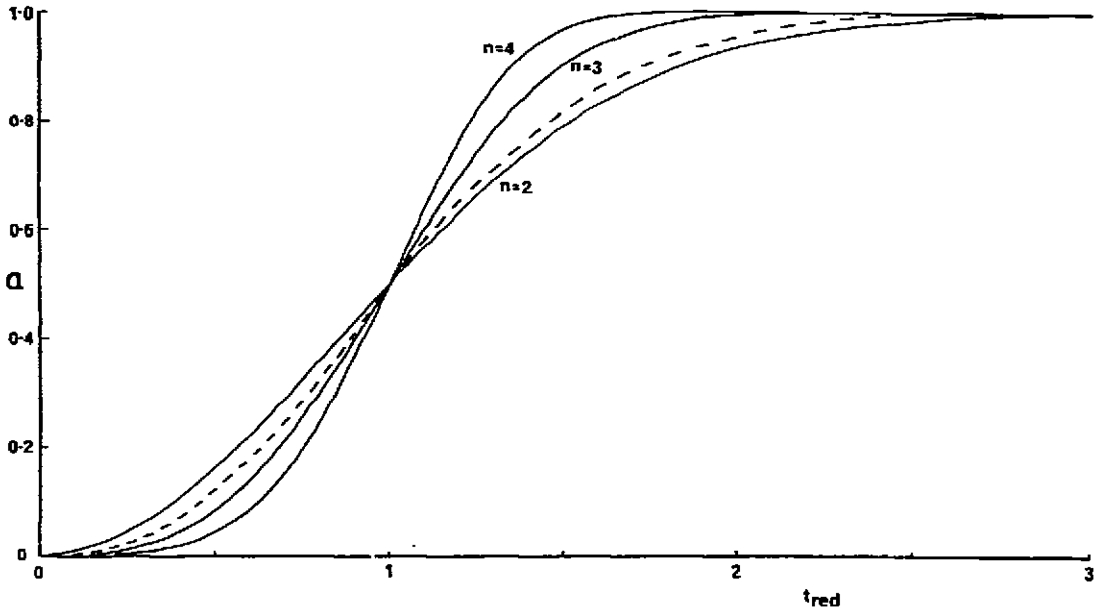


Fig. 8. Experimental (— — —) and theoretical (Avrami—Erofeev) reduced-time curves for the $Hg(NT)_2$ decomposition.

above. Rate coefficients $k_{n2.5}$ and $k_{n3.5}$ ($0.05 < \alpha < 0.5$) and k_{n2} and $k_{n2.5}$ ($0.5 < \alpha < 0.95$) were thus evaluated at each temperature. Arrhenius plots then gave the apparent activation energies, E_a, and frequency factors, A, listed in Table 4.

Decomposition in an atmosphere of oxygen at 450 K did not markedly affect the α—time curve obtained, but slightly increased the overall mass loss (90.5% compared with 86 ±1%).

A DSC run on $Hg(NT)_2$ in nitrogen at 10 K min^{-1} showed that decomposition is strongly exothermic (Fig. 9). The overall enthalpy of decomposition was estimated, by comparison with the melting endotherm of pure indium metal, as −890 ±40 kJ $mole^{-1}$ (or −2.07 ±0.09 kJ g^{-1}). The shoulder on the exotherm may be caused by an endothermic contribution from the vaporiza-

TABLE 4

Apparent Arrhenius parameters for the thermal decomposition of $Hg(NT)_2$ in argon (438—461 K)

	E_a/kJ $mole^{-1}$	$\ln(A/min^{-1})$	Correlation coefficient
Acceleratory period			
Avrami, $n = 3.5$	160 ± 11	39.4	0.9931
$n = 2.5$	160 ± 12	39.5	0.9910
Decelaratory period			
Avrami, $n = 2$	137 ± 19	33.5	0.9728
$n = 2.5$	137 ± 19	33.2	0.9713

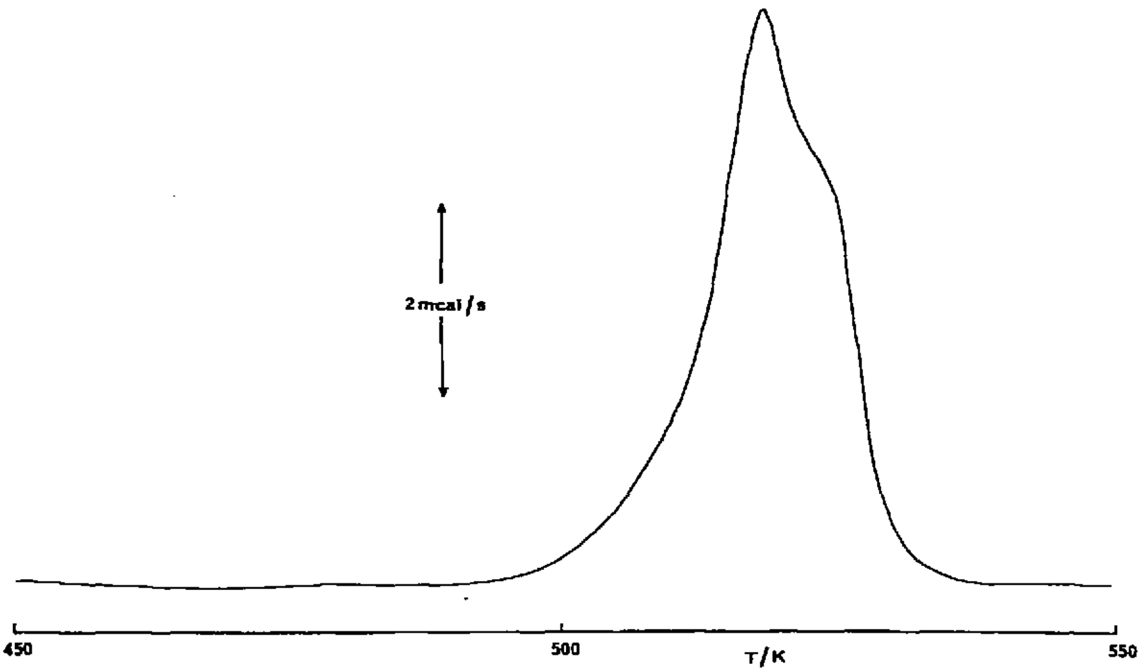


Fig. 9. DSC trace for $Hg(NT)_2$ (0.48 mg) in nitrogen at 10 K min^{-1}.

tion of product mercury ($\Delta H_{vap,Hg} \simeq$ 59 kJ $mole^{-1}$ around 500 K).

Hot stage optical microscopy in transmitted light showed little change in the crystallites, other than the change from colourless to reddish-orange, during decomposition. Scanning electron microscopy showing that the product was extensively cracked across the plate-like crystallites, parallel to the longest dimension (Fig. 10). Such cracking produces a greatly increased surface area on which decomposition can occur with easy escape of product gases and can account for the observed acceleratory behaviour [8].

The infrared spectrum of $Hg(NT)_2$ in a nujol mull (2000—600 cm^{-1}) contained strong multiple absorptions at about 1550, 1330 and 850 cm^{-1} (these were also present in the spectrum of AgNT). None of these peaks was present in the spectrum of the product of the $Hg(NT)_2$ decomposition.

Mercury(II) fulminate [$Hg(CNO)_2$]

Because of the large mass losses (~85%) observed in the study of the thermal decomposition of $Hg(NT)_2$ using thermogravimetry (438—461 K), which indicate the evolution of mercury or volatile mercury compounds in the gaseous products, it was thought to be of interest to re-examine some aspects of the thermal decomposition of the well-known detonant mercury(II) fulminate. The properties of $Hg(CNO)_2$ have been extensively studied, but kinetic studies of the thermal decomposition have apparently been carried out only by measurement of the pressure of gases evolved into an initially evacuated, constant volume apparatus. In such systems, the manometer was usually a McLeod gauge so that any mercury, or conden-

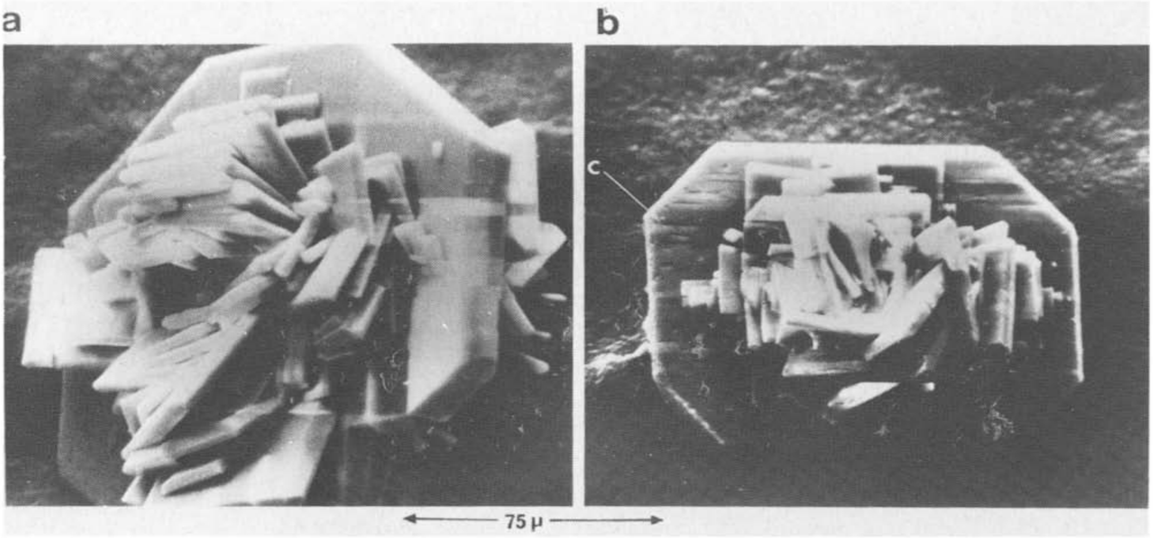


Fig. 10. Electron micrographs of $Hg(NT)_2$ (a) before and (b) during decomposition showing formation of cracks (c).

sable mercury compound, evolved during decomposition would not be detected. The reported [9—11] temperature range for thermal decomposition in low pressures of evolved gas is 340—390 K, which is lower than the temperature range (440—460 K) required for decomposition of $Hg(NT)_2$ in argon.

Preliminary TG runs on small (<1 mg) samples of $Hg(CNO)_2$ powder showed that, at a heating rate of 10 K min^{-1} (and 50 ml min^{-1} of argon), decomposition began at about 390 K followed shortly by explosion. Reducing the heating rate to 5 K min^{-1} and holding at 393 K successfully induced non-explosive decomposition with a mass loss of about 25%, which is only slightly greater than the 23.9% expected for

$$Hg(CNO)_2(s) \rightarrow HgO(s) + \text{gases}$$

Further mass losses occur on continued heating to above 440 K. On heating at 5 K min^{-1} in an atmosphere of oxygen, a decomposition stage similar to that in argon occurred.

Hg_2O is reported [12] as decomposing above 373 K and HgO around 670 K in a deceleratory reaction [13] with $E_a = 162$ kJ $mole^{-1}$ for fine powder and 200 kJ $mole^{-1}$ for larger crystals. The enthalpy of dissociation of HgO is approximately 160 kJ $mole^{-1}$. The dissociation is inhibited [14] by both mercury and oxygen, with mercury having the greater effect. The vapour pressure of mercury [12] is 1 mm at 399 K, rising to 10 mm at 457 K, 100 mm at 535 K and 760 mm at 630 K. Mercury, but no higher mass mercury compound, was detected in the mass spectra of the gaseous products of $Hg(CNO)_2$ decomposed directly in the mass spectrometer.

A series of isothermal runs spanning the range 380—399 K in argon (50 ml min^{-1}) gave sigmoid curves similar to those of $Hg(NT)_2$. On a reduced-time scale ($t_{red} = t/t_{0.5}$), these curves were coincident (Fig. 11) and conformed most closely to the Avrami—Erofeev model with $n = 4$. The mass losses observed were 17 ±2% of the original sample mass.

Plots of $\{-\ln(1-\alpha)\}^{1/n}$ against t for $n = 2$, 4 and 6 were made. The least-square slopes of the approximately linear regions of the plots for $n = 4$ and $n = 6$ were used as estimates of the rate coefficients. Arrhenius plots of these rate coefficients gave apparent activation energies of 136 ±15 kJ mole^{-1} ($n = 4$) and 133 ±14 kJ mole^{-1} ($n = 6$). The corresponding frequency factors, $\ln(A/\text{min}^{-1})$, were 38.4 and 37.1, respectively.

Bowden and Yoffe [11] quote a value of 135 kJ mole^{-1} for the activation energy, while Garner and Hailes [15] report that the acceleratory period for the decomposition of whole crystals is fitted by

$$\log \{(\mathrm{d}\alpha/\mathrm{d}t) - (\mathrm{d}\alpha/\mathrm{d}t)_0\} = k(t - t_0)$$

with an activation energy of 130 kJ mole^{-1}. Vaughan and Phillips [16] applied the Prout—Tompkins equation to their results for decomposition of "service" material and the activation energy was 107 kJ mole^{-1}. Their results were reanalysed by Garner and Haycock [17] and were shown to conform closely to

$$(\alpha - \alpha_0)^{1/3} = k(t - t_0)$$

with unchanged activation energy. The inflexion point of the sigmoid curve was reported [16] as moving to higher values of α with increasing temperature (0.5 at 348 K but 0.75 at 367 K).

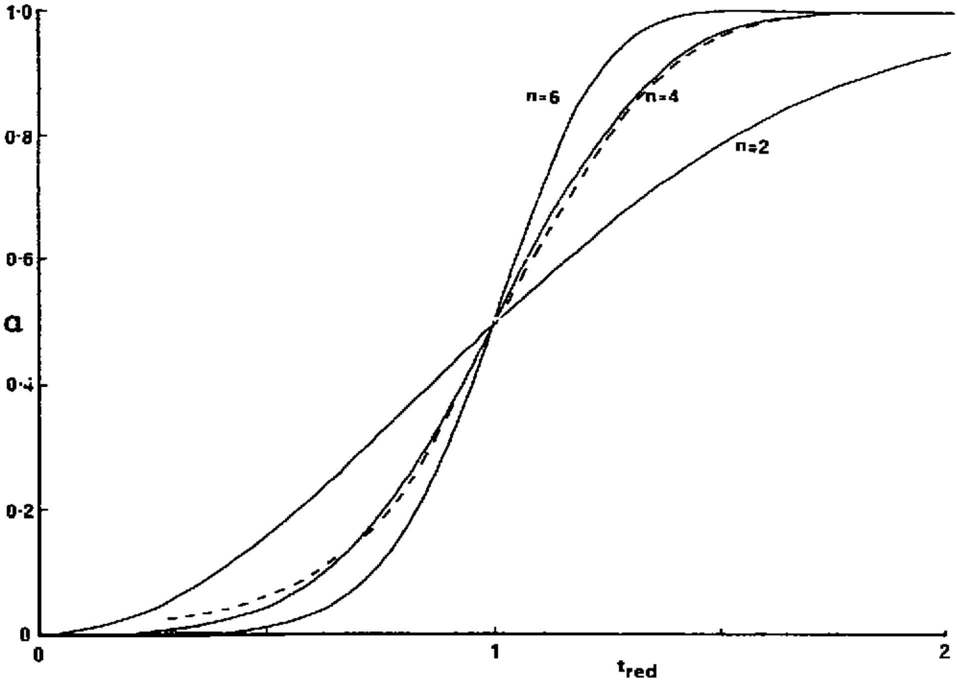


Fig. 11. Experimental (— — —) and theoretical (Avrami—Erofeev) reduced-time curves for the $Hg(CNO)_2$ decomposition.

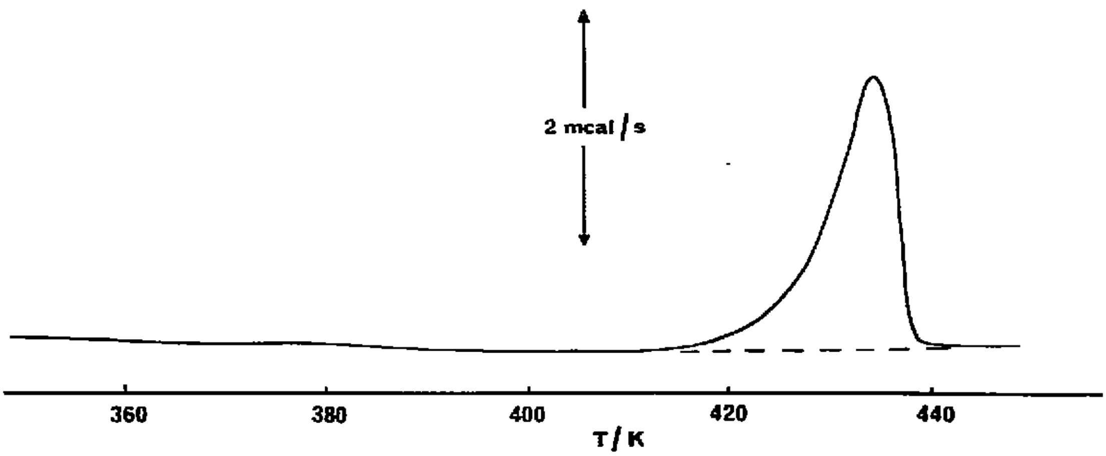


Fig. 12. DSC trace for $Hg(CNO)_2$ (0.65 mg) in nitrogen at 2.5 K min^{-1}.

A DSC scan on $Hg(CNO)_2$ (Fig. 12) shows onset of exothermic decomposition at about 410 K with an enthalpy of decomposition of —430 ±10 kJ $mole^{-1}$ (—1.52 ±0.03 kJ g^{-1}).

Examination while heating on the hot stage of the optical microscope showed that crystals shatter violently (around 420 K) into irregular fragments. Scanning electron microscopy (Fig. 13) shows the irregularly channeled residue. It appears as if reaction proceeds along channels into the crystal with possible intersection and branching. Build-up of gaseous products coupled with the heat evolved on decomposition, causes undecomposed fragments to be blown off the larger crystallites. The residue, while sometimes retaining the external shape of the reactant, is amorphous to X-rays.

The infrared spectrum (2500—900 cm^{-1}) of $Hg(CNO)_2$ in a nujol mull showed strong adsorptions at about 2200 cm^{-1} and 1200 cm^{-1}. These were not observed in the spectrum of the product.

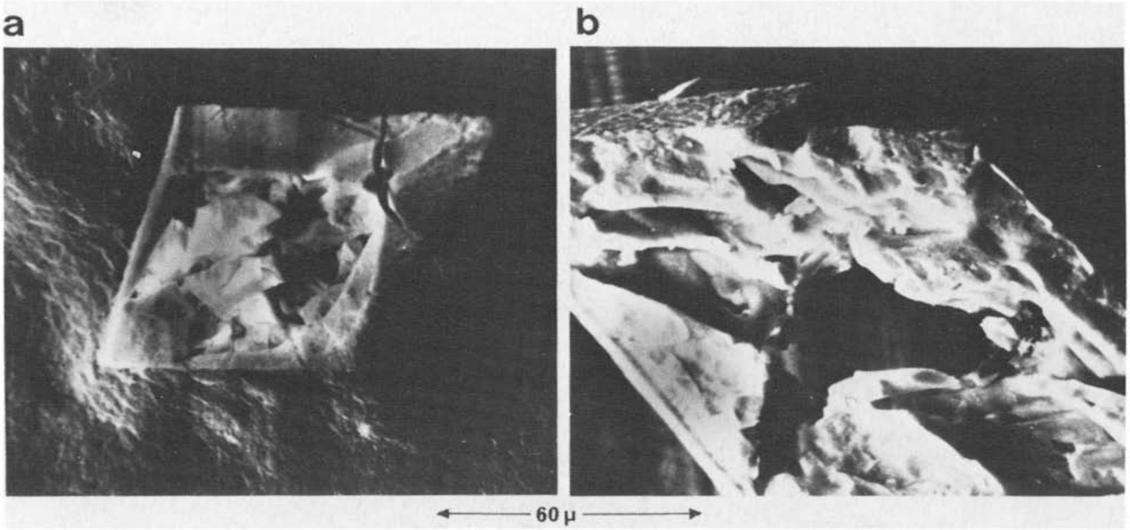


Fig. 13. Electron micrographs of $Hg(CNO)_2$ (a) during and (b) after decomposition.

TABLE 5

Kinetic and thermodynamic parameters for the thermal decomposition of several detonatants

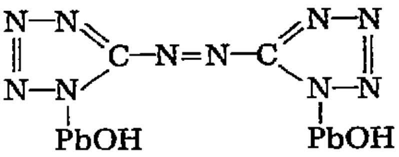
	Enthalpy of decomposition		Arrhenius parameters	
	kJ mole^{-1}	kJ g^{-1}	E_a/kJ mole^{-1}	ln(A/min^{-1})
$Hg(CNO)_2$ (380—400 K)	—430 ± 10	—1.52 ± 0.03	136 ± 15	38.4
$Hg(NT)_2$ (440—460 K)	—890 ± 40	—2.07 ± 0.09	160 ± 11 137 ± 19	39.4 33.5
AgNT (485—525 K)	—430 ± 20	—1.94 ± 0.10	246 ± 24 166 ± 11	56.3 37.8
α-PbN_6 *	—480	—1.65	159	
β-PbN_6 **			163 ± 8	29.9

* Ref. 11.
** Ref. 19.

In an attempt to see if the decomposition of $Hg(NT)_2$ could be accelerated by the presence of active species produced by the decomposition of the fulminate, TG runs at a heating rate of 4.5 K min^{-1} and DSC runs at 5 K min^{-1} were carried out on samples containing 10% by mass of the fulminate and 90% of the nitrotetrazole. Two exothermic decomposition regions of the correct mass loss ratios and enthalpy values (as determined from the decomposition of pure samples) and separated by approximately 60 K were observed. The decompositions of the nitrotetrazole and the fulminate thus proceed independently and it must be assumed that no species produced in the fulminate decomposition is active in inducing or catalysing the decomposition of the nitrotetrazole.

CONCLUSIONS

Mercury(II) nitrotetrazole [$Hg(NT)_2$] is more stable to heat than mercury(II) fulminate [$Hg(CNO)_2$], decomposing at 440—460 K compared with 380—400 K. Both yield similar solid residues, probably amorphous HgO, although the quantity of residue from the $Hg(NT)_2$ decomposition is far less than that expected from stoichiometry. The measured activation energy of 160 kJ mole^{-1} for the early stages of $Hg(NT)_2$ decomposition is the same as the enthalpy of dissociation of HgO, while the value of 137 kJ mole^{-1} for the later stages of the $Hg(NT)_2$ decomposition is similar to that for the decomposition of $Hg(CNO)_2$. It is possible that both decompositions lead to HgO as product, but that, at the higher temperature of the $Hg(NT)_2$ decomposition, the HgO is unstable and dissociates giving rise to a complicated set of concurrent processes including possible catalytic or inhibiting effects of Hg and O_2 [13,14]. The possibility of the formation of some, as yet unidentified, volatile organometallic compound of mercury cannot be excluded as the decomposition of lead azotetrazole [18] (LAT)



over the temperature range 480—500 K [which is well below even the melting point of lead (600 K)] resulted in an unexplained mass loss of 67% compared with the 32.4% expected for a lead residue alone.

Silver(I) nitrotetrazole (AgNT) decomposed at temperatures (485—525 K) above those required for decomposition of the mercury salts. Decomposition is accompanied by melting with the formation of a sintered silver metal product. The measured activation energies were higher than for the mercury salts, being 246 kJ mole^{-1} for the initial stages (corresponding to solid state decomposition) reducing to 166 kJ mole^{-1} in the later stages. This lowering may be due to the melting process and/or a catalytic effect of the metal product formed.

The decompositions of all three compounds are strongly exothermic. Enthalpy values are summarized in Table 5, together with the Arrhenius parameters and the corresponding values for lead azide [11,19]. The nitrotetrazole salts evolve up to 25% more heat per unit mass than mercury fulminate or lead azide. Activation energies are similar. A study of the initiation and propagation of detonation in these nitrotetrazole salts is in progress.

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