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THE RELATIONSHIP BETWEEN IGNITION TEMPERATURE AND THERMAL STABILITY FOR SELECTED PRIMARY EXPLOSIVES

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ABSTRACT

Thermal stability of nine primary explosives has been determined at 89°C. Half-lives ($t_{1/2}$) for thermal decomposition are correlated against temperature of ignition (T_I) and the peak maxima (T_{max}) in the DSC traces. A trend to increased thermal stability with increased T_I and T_{max} is observed, with T_{max} giving the better correlation. Thermal decomposition of three of the materials is accompanied by a decrease in T_{max} by up to 10°C at 50% decomposition. This could be an indication of autocatalytic decomposition.

INTRODUCTION

One of the key parameters for characterization of explosive materials is ignition temperature. Many methods exist for experimental determination of ignition temperature with the most commonly used being the ERDE Temperature of Ignition (T_I) Test. This method consists of heating unconfined samples of 50 mg at a controlled rate of 5°C min^{-1}, the T_I being that temperature at which the samples ignited to explosion or fast burn.

Although primarily a safety screening test, since it measures the temperature at which a material will undergo runaway exothermic decomposition, the assumption is frequently made that T_I is a measure of thermal stability. For many applications involving primary explosive materials, both ignition temperature and thermal stability are important. One such area of investigation is stab and percussion primer mixes, where the primary explosive tetrazene is used almost universally to impart the high sensitivity to these mixes. We have carried out extensive investigations on materials suitable for replacing tetrazene, specifically searching for materials which possess better thermal stability than tetrazene coupled with comparable sensitizing ability. The latter property is dependent on T_I, with lower T_I leading to enhanced sensitization [1,2]. Thus, if there is a direct correlation between ignition temperature and thermal stability, more thermally stable materials would be expected to have decreased sensitizing ability.

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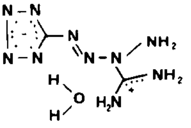
The aim of the work reported here was principally to examine the relationship between thermal stability and ignition temperature for a selected group of primary explosives. A further aim was to identify promising materials which exhibited good sensitizing ability (in stab mixes) coupled with greater thermal stability than tetrazene.

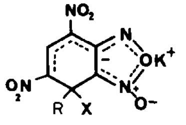
EXPERIMENTAL

Materials

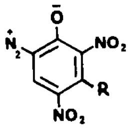
A total of nine compounds whose structures are shown below as (**1**) – (**9**) were chosen for this study. Selection of compounds was based on two criteria; compounds (**3**), (**4**), (**5**), (**7**) and (**9**) were chosen because they showed excellent promise as sensitizing agents and their thermal stability was being assessed against tetrazene (**1**), while the remainder were included to give a range of T_I of about 130–200°C.



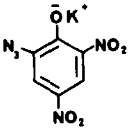
TETRAZENE (1)



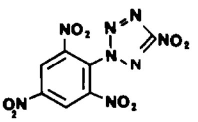
R	X	
H	OH	(2)
H	NHOH	(3)
=N — OH		(4)



R = H (5)
R = CH$_3$ (6)
R = Cl (7)



(8)



(9)

Tetrazene (**1**) was type RD1357. The other materials included three potassium complexes derived from 4,6-dinitrobenzofuroxan, namely the 4-hydroxy (**2**), 4-hydroxylamino (**3**) and 4-oximo (**4**) derivatives, and 2-diazo-4,6-dinitrophenolate (**5**) and its 5-methyl (**6**) and 5-chloro (**7**) derivative. Potassium 2-azido-4,6-dinitrophenolate (**8**), a compound prepared from (**5**), and 2-picryl-5-nitrotetrazole (**9**), were the final materials studied. All these compounds have been described previously by us [1–3]. Three are currently used in explosive compositions: tetrazene (**1**) is the sensitizer used almost exclusively in stab and percussion mixes, while (**2**) is used under the name KDNBF and (**5**) is known as DDNP.

METHODS

Temperature of ignition (T_I*)*

T_I was determined on an instrument built to specifications for the ERDE temperature of ignition test *. As mentioned in the introduction, unconfined 50 mg samples were heated at 5°C min^{-1} in test tubes, the temperature of ignition being that temperature at which the samples ignited to explosion or fast burn. Measurements were performed in triplicate and results were reproducible to within ±1°C.

Procedure for thermal stability testing

Thermal stability was investigated using a Qualtex Solidstat oven, model OG18SZ. The oven settings were adjusted to an average temperature of 89.0°C. Measurements with a pre-calibrated digital thermometer positioned on the same shelf as the experimental samples showed that the temperature cycled each 3.70 ± 0.15 min over a maximum temperature range of 88.4–89.6°C, with a typical temperature range of 88.6–89.4°C.

The samples for thermal testing consisted of about 0.2 mg weighed accurately (to 0.001 mg), using a Mettler ME 30 Microbalance, directly into aluminium DSC sample pans. Each pan was then placed in a numbered position in an aluminium sample holder which held 20–30 pans. The holders were each loosely covered with a cardboard sheet and placed in the oven.

Samples were removed at regular intervals for analysis. Weight loss and analysis by DSC was carried out on the day of sampling.

Differential scanning calorimetry (DSC)

Thermochemical measurements were obtained using a Perkin–Elmer DSC–2 differential scanning calorimeter fitted with a Scanning Auto-Zero (SAZ) accessory. The sample and reference compartments of the calorimeter were continuously purged with nitrogen gas throughout the DSC scans, which were carried out at a heating rate of 20°C min^{-1} over the temperature range 320 to 600 K. The nitrogen flow rate was typically 20–25 ml min^{-1}. Lids were placed (not crimped) on the samples. The output was calibrated using samples of indium (m.p. 429.7 K) and tin (m.p. 505.1 K).

The choice of sample size and heating rate resulted from a consideration of the susceptibility of these materials, when in larger masses and at higher heating rates, to undergo rapid thermal decomposition. When a large output of heat was generated too quickly, loss of thermal equilibrium could occur

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* ERDE was renamed PERME in 1977, and is now called RARDE (Waltham Abbey).

and the DSC "peak" would often run "off scale". This probably corresponded to "ignition" followed by "thermal explosion"; in most of these cases, the sample lid was blown off the pan in the DSC sample compartment. Even so, compound (**6**) still exhibited a high proportion of "off-scale" traces, which necessitated scanning at 10°C min^{-1}.

Analysis of thermally degraded samples was carried out in duplicate. Peak areas were determined by digitization. In the case of materials such as tetrazene (**1**), where two non-overlapping exotherms were present, only the area of the lower temperature exotherm was determined. The proportion of material remaining in each sample was calculated from the relative areas of DSC traces from pure control samples.

RESULTS AND DISCUSSION

Although the derivation of the thermal stability test used here has been reported previously [4], it was felt that some comment should be made on the choice of temperature. The thermal decomposition of tetrazene has been fairly extensively studied [5–8], but there is considerable variation in the quoted decomposition rates. Norwitz et al. [5] studied two different commercial batches of tetrazene and found one batch "deteriorated" in 5 weeks at 60°C, 8 days at 75°C and 3 h at 100°C, while the corresponding values for the other batch were > 13 weeks, 14 days and 7.5 h respectively. In contrast Bird et al. [7,8] state that tetrazene decomposes too slowly at 60°C for short-term experimentation, can withstand 75–80°C for short periods, while at 90°C decomposition is complete within one week. Reitsma [9] has reported that tetrazene is recovered unchanged after 91 days at 65°C. A temperature of about 90°C was accordingly chosen; at this temperature complete decomposition of tetrazene should be expected within 1 month, and any enhanced thermal stability of other materials should thus be readily apparent.

Thermal decompositions were followed in most cases to about 80% decomposition. All samples lost weight due to the formation of volatile products. Reaction half-lives ($t_{1/2}$), determined by plotting residual content against time, are listed for (**1**)–(**9**) in Table 1. The $t_{1/2}$ figures are believed to be accurate under these experimental conditions to better than 5%. The value for (**2**) is an estimate obtained by extrapolation since only about 10% decomposition had occurred after 200 days.

Values of T_{I} for (**1**)–(**9**) are also listed in Table 1, along with temperature maxima from the DSC exotherms (T_{max}) both for the pure and 50% decomposed materials. A plot of $t_{1/2}$ against both T_{I} and T_{max} (pure material) is shown in Fig. 1; points for compound (**2**) are not included.

The relationship between T_{I} and $t_{1/2}$ (Fig. 1) clearly indicates a trend to increasing thermal stability with increasing T_{I}. However one would hesitate

TABLE 1

Thermal parameters for primary explosives (1)–(9)

Material	Thermal decomposition half-life ($t_{1/2}$, days)	Temperature of ignition (T_I) (°C)	DSC peak maxima (°C) [a]	
			Pure sample	Sample thermally decomposed to 50% purity
(1)	17	136	150	148
(2)	> 360	200	231	not determined
(3)	16.5	136	167	167
(4)	85	140	176	171
(5)	50	157	178	178
(6)	155	183	201 [a] 193 [b]	182 [b]
(7)	185	178	203	204
(8)	< 1	133	149	not determined
(9)	75	166	173	162

[a] Determined at 20°C min^{-1} scanning rate unless stated otherwise.

[b] Determined at 10°C min^{-1} scanning rate (see note in Experimental section).

to use the relationship as a prediction of service lifetimes. For example, compound (4) is considerably more stable than its low T_I would suggest; certainly an increase in $t_{1/2}$ from the approx. 17 days for (1) and (3) to 85 days for (4) would be important for practical use. The correlation between T_{max} and $t_{1/2}$, also plotted in Fig. 1, is better than for T_I. The respective correlation coefficients are 0.90 and 0.79, hence the relation between $t_{1/2}$

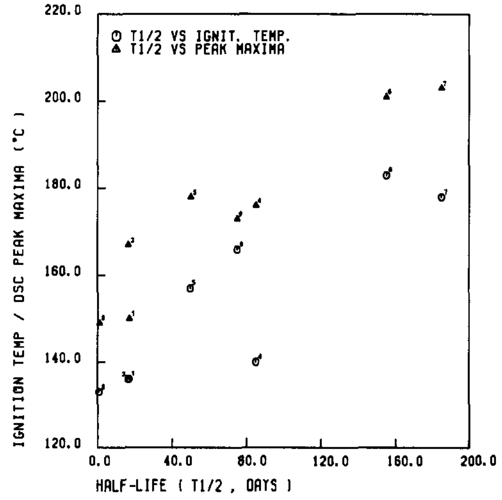

Fig. 1. A plot of half-life for thermal decomposition against T_I (⊙) and DSC exotherm peak maxima (▲) for primary explosives (1) and (3)–(9). Data for (2) are omitted since they would lie well off-scale.

and T_{max} is still qualitative. The better correlation between $t_{1/2}$ and T_{max} is probably to be expected since both thermal stability and T_{max} are recorded on samples of nearly identical mass, and a strong dependence between thermal stability and sample mass has been noted previously for both tetrazene (**1**) [4,7,8] and PNT (**9**) [4]. However neither the plot of T_I nor T_{max} versus $t_{1/2}$ gives a reliable result when extrapolated for (**2**); both predict a half-life of about 250 days which is considerably below the estimated value of 360 days.

The relationship between T_I and T_{max} (at 5°C min^{-1}) has been described previously by us [2,3]. In general, T_{max} values are higher, reflecting the DSC conditions where thermal equilibrium is maintained rather than the runaway thermal explosions of the temperature of ignition test. In all the compounds studied here, the DSC traces used to obtain the residual purity exhibit increased broadness of the exotherm with increased decomposition. In many cases T_{max} remains constant despite the increased broadness, but in some instances, notably (**6**) and (**9**) and to a lesser extent (**4**), T_{max} decreases with time (Table 1).

The decrease of T_{max} with time could have important consequences for safe-handling of these materials since thermal sensitivity, i.e., the tendency to ignition, increases with decreasing T_I. Whether this indicates that (**4**), (**6**) and (**9**) may be subject to autocatalytic decomposition, the major hazard for storage of nitrocellulose and related materials, cannot be answered from the data reported here. However, data available on thermal decomposition of larger masses of (**9**) [4] suggest that autocatalysis is occurring.

A final comment should be made on the unexpectedly poor thermal stability of (**8**). Aryl azides can undergo thermolysis at temperatures as low as 90°C [10], but the extremely facile thermolysis observed for (**8**) was unexpected. The structure of the reaction products have as yet not been determined, and we are currently investigating the thermal decomposition reaction.

CONCLUSIONS

A trend towards increased thermal stability with increasing T_I has been demonstrated for a series of primary explosives. A better correlation is obtained if T_{max} from the DSC exotherm is used. Both T_I and T_{max} are readily measurable parameters, and T_{max} should therefore give a more reliable estimate of thermal stability. The poor correspondence between the predicted half-life for KDNBF (**2**) and the value estimated from the experimental data suggests that extrapolation to materials with higher ignition temperatures would not give reliable estimates. Three of the materials studied here, namely potassium 4-hydroxylamino-5,7-dinitrobenzofurazanide 3-oxide (**4**), 2-diazo-4,6-dinitro-5-methylphenolate (**6**) and 2-picryl-5-

nitrotetrazole (**9**), exhibit decreasing values of T_{max} with increasing thermal decomposition. This suggests that autocatalysis may be occurring, and has important implication for the safe-handling of these materials. Further investigations into this behaviour are being undertaken.

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