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Temperature calibration in thermogravimetry using energetic materials

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Abstract

Compounds which undergo strongly exothermic decompositions (some molybdenum peroxo complexes in this study) were investigated as possible temperature calibrants in thermogravimetry (TG). Onset temperatures of these exothermic reactions were determined using a differential scanning calorimeter (DSC) which had been calibrated on the melting points of standard materials. These onset temperatures in the DSC were compared with the onset temperatures of the explosive reactions of small samples in the TG. Details of the preparation of the complexes used are given, but it is expected that suggestions for other suitable substances will be forthcoming.

Keywords: Calibration; Coupled technique; DSC; Explosive; Molybdenum compound; Peroxide; TG

1. Introduction

Accurate determination of the sample temperature in thermogravimetry (TG) is a major problem [1], especially in the lower temperature region (50–150°C, say). The main calibration procedure used is based on the detection of the Curie transitions of magnetic materials [2, 3]. Use has also been reported of the weighing disturbance caused by the melting of fusible links [4, 5].

Temperature calibration in DSC [6] or DTA studies is not as much of a problem because there are many substances for which the thermal effects associated with

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melting transitions may be used. Some are more reliable as references than others, but nearly all provide a better basis than the TG calibrants. These transitions are only detectable through their thermal effects as there is no simultaneous mass change. Balek et al. [7] have recently published a literature survey of reference materials.

Charsley et al. [8] have used a Stanton Redcroft simultaneous TG–DTA instrument, calibrated using the DTA response to melting of pure metals, to determine accurate temperature values for the Curie transitions of the ICTAC reference materials. Zhong and Gallagher [9] carried out a similar, but more extensive study using a Seiko TG/DTA330 apparatus.

Many solid substances decompose or react with the surrounding atmosphere in processes involving both mass change and absorption or evolution of energy. These processes often have Arrhenius parameters in a range such that reactions take place at measurable rates over a wide range of temperatures. Considerable effort has been put into the search for a "kinetic standard" [10], especially into the possible use of the dehydration of $Li_2SO_4 \cdot H_2O$ as a reference reaction, but there has so far been little success. If such a standard were available, reliable measurements of rates could be used to calibrate the temperature in the apparatus used.

Rates of reactions involving solids are, however, notoriously dependent on many factors which are difficult to control, such as particle size and distribution, reactant pre-treatment, self-heating or self-cooling, etc. [11].

In this paper, the possibility of using very small samples of materials which undergo strongly exothermic, high activation energy reactions as calibrants is considered. Such substances would be extremely unsuitable as kinetic standards, but could have value in defining the sample temperature in a given TG apparatus. The particular compounds considered are some molybdenum peroxo complexes, but many other energetic materials may prove suitable.

2. Experimental

### 2.1. Preparation of the metal-peroxo complexes

2.1.1. Materials

Potassium molybdate (K_2MoO_4), (+)-tartaric acid, malonic acid and glycine (all Fluka reagents) were recrystallized from hot water (tart is $C_2H_4O_6^{2-}$, mal is $C_3H_2O_4^{2-}$, and gly is $NH_2C_2H_2O_2^-$).

The method used in the preparation of the tartrate and malonate complexes is that reported by Griffith et al. [12] with some modifications in the crystallization stage [13].

$K_2[MoO(O_2)_2(tart)] \cdot 2H_2O$
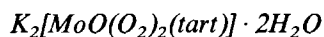
K_2MoO_4 (2.0 g, 8.4 mmol) and (+)-tartaric acid (1.26 g, 8.4 mmol) were dissolved in water (15 cm^3) and the solution stirred at room temperature for 10 min.
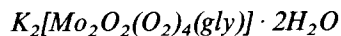
30% H_2O_2(10 cm³) was then added dropwise, with stirring, to give a yellow solution. The solution (pH 2.5–2.7) was stirred for a further 10 min at room temperature. Addition of ethanol (40–50 cm³) produced an oily residue and the reaction vessel was then kept at ice-bath temperature overnight. The crystalline material that resulted was filtered, washed with ethanol (3 × 5 cm³) and air-dried under suction. The yield was 48%.

$K_2[Mo_2O_2(O_2)_4(tart)] \cdot 4H_2O$
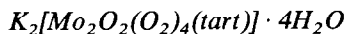
This complex was prepared as above [12], but at pH 4.0, with a K_2MoO_4:L ratio of 2:1.

$K_2[Mo_2O_2(O_2)_4(mal)] \cdot 2H_2O$
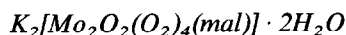
The procedure was as described above, but using malonic acid (0.87 g, 8.4 mmol) and a K_2MoO_4:L ratio of 2:1. The resulting clear yellow solution (pH 3.6–3.8) was stirred for a further 10 min. Addition of ethanol (30 cm³) followed by slight scratching of the vessel produced yellow crystals. The reaction vessel was then left at ice-bath temperature overnight. The yellow microcrystalline product was filtered, washed with ethanol (3 × 5 cm³) and air-dried under suction. The yield was 28%.

$K_2[Mo_2O_2(O_2)_4(gly)] \cdot 2H_2O$

K_2MoO_4 (2.0 g, 8.4 mmol) was dissolved in H_2O (15 cm³) and the solution stirred at 0°C for 10 min. 30% H_2O_2 (5 cm³) was then added dropwise with stirring and gave a deep red solution. Stirring was continued for 5 min, after which the ice-bath was removed and the ice-cold solution gradually treated with glycine (0.63 g, 8.4 mmol). The solution, pH 8.6–8.8, was stirred for a further 10 min. The pH was then adjusted to ≈4.0 to give a yellow solution. Treatment with ethanol (30 cm³) precipitated yellow microcrystals which were filtered, washed with ethanol (3 × 5 cm³) and then ether (2 × 5 cm³), and air-dried under suction. The yield was 49%.

2.1.2. General properties

Infrared spectra were recorded as mulls in liquid paraffin between potassium bromide plates. Peroxide analyses were by iodometric titration. Potassium was determined by atomic absorption spectrophotometry. C, H and N analyses were performed by the FRD, Pretoria. The results of the elemental analyses are given in Table 1.

The complexes decompose via the loss of peroxide when exposed to light, even at room temperature. They can be kept in a refrigerator (0 to −10°C) for months without any detectable loss of peroxide. Decomposition occurs with no detectable melting.

The IR spectra of the complexes show the four significant vibrations expected of peroxo compounds [14, 15]. These are the metal–oxygen (M=O) stretch (980–

Table 1
Elemental analyses

Complex	C/%		N/%		H/%		K/%		$(O_2)^{2-}$/%	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
$K_2[MoO(O_2)_2(tart)] \cdot 2H_2O$	11.00	11.24	–	–	1.83	1.74	17.85	17.72	14.62	14.41
$K_2[Mo_2O_2(O_2)_4(tart)] \cdot 4H_2O$	7.38	7.29	–	–	1.85	1.77	12.03	12.12	19.69	19.49
$K_2[Mo_2O_2(O_2)_4(mal)] \cdot 2H_2O$	6.45	6.34	–	–	1.06	0.90	14.01	13.44	22.53	22.64
$K_2[Mo_2O_2(O_2)_4(gly)] \cdot 2H_2O$	6.66	6.81	2.59	2.19	2.04	2.01	14.48	14.22	23.70	23.19

900 cm^{-1}), the peroxo stretchings (O–O) (900–800 cm^{-1}), and the symmetric-asymmetric (MO$_2$) stretchings, usually found below 700 cm^{-1} [15]. The bands in the region 1630–1580 cm^{-1} corresponding to antisymmetric (CO$_2$M) vibrations (bound carboxyl group) suggest [16] that the organic acids are coordinated to the metal via the oxygen atoms which result after deprotonation. More detail of the structural aspects and reactivity of these and related complexes is to be published [13].

2.2. Equipment and procedure

All thermal analysis experiments were carried out on a Perkin-Elmer Delta Series 7 TG and DSC. Very small samples (<2 mg) were used and samples were heated in open platinum pans (TG) and covered, but uncrimped, aluminium pans (DSC). The atmosphere was flowing nitrogen (60 cm^3 min^{-1}).

The temperature scale of the DSC had been calibrated in the normal fashion, using the melting points of indium and zinc metals, and the TG was calibrated using the Curie points of Ni and Fe.

3. Results

DSC runs on the molybdenum peroxo complexes showed very sharp exotherms under most conditions. The onset temperatures of these exothermic "spikes", estimated from the intersection of the extrapolated steep slope of the exotherm with the baseline, were very reproducible (at most ±1°C).

TG runs on samples of the same compounds, heated under similar conditions, under most conditions showed an explosive loss of mass at a reproducible onset temperature (estimated as above) which can logically be assumed to be very close to that observed in the DSC. On this assumption, the recorded TG temperatures can be corrected to match the calibration of the DSC. The explosive mass losses are far sharper than the apparent weight losses recorded during Curie transitions. Under some conditions (usually slow heating rates and very small sample masses), ignition did not occur (see Table 2).
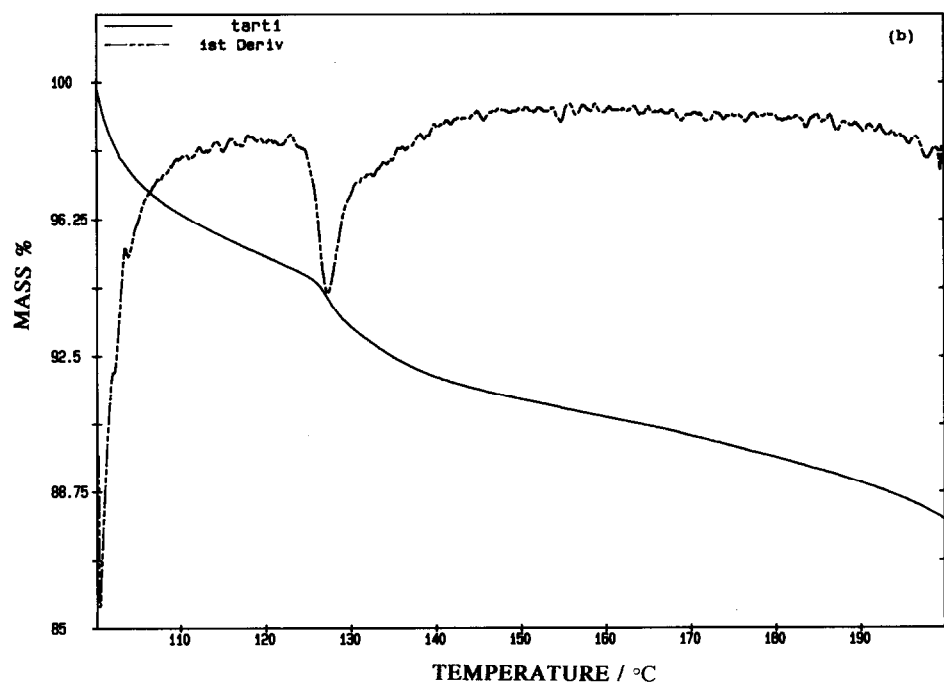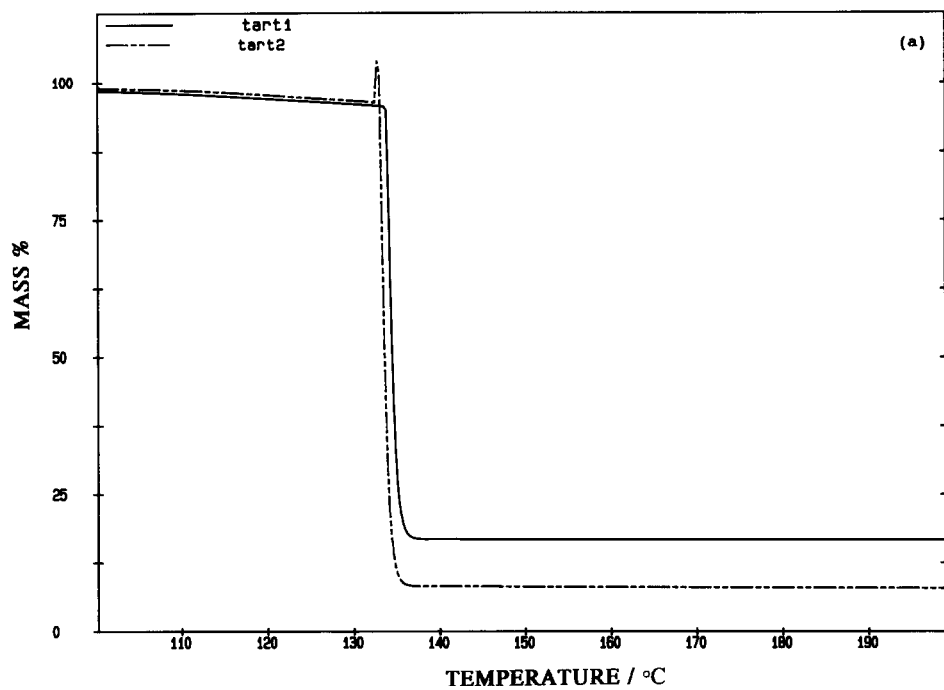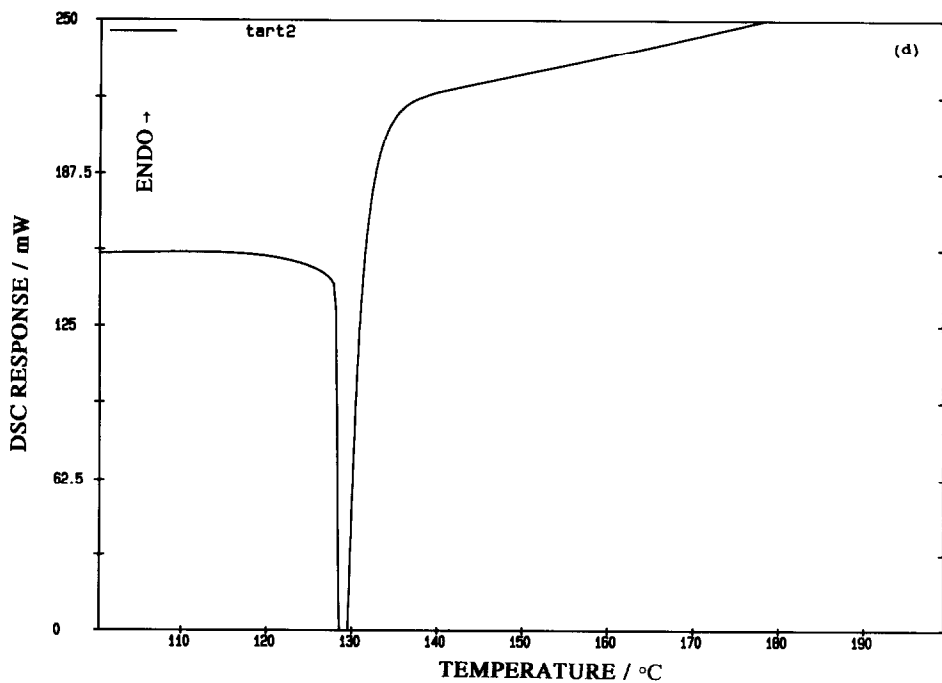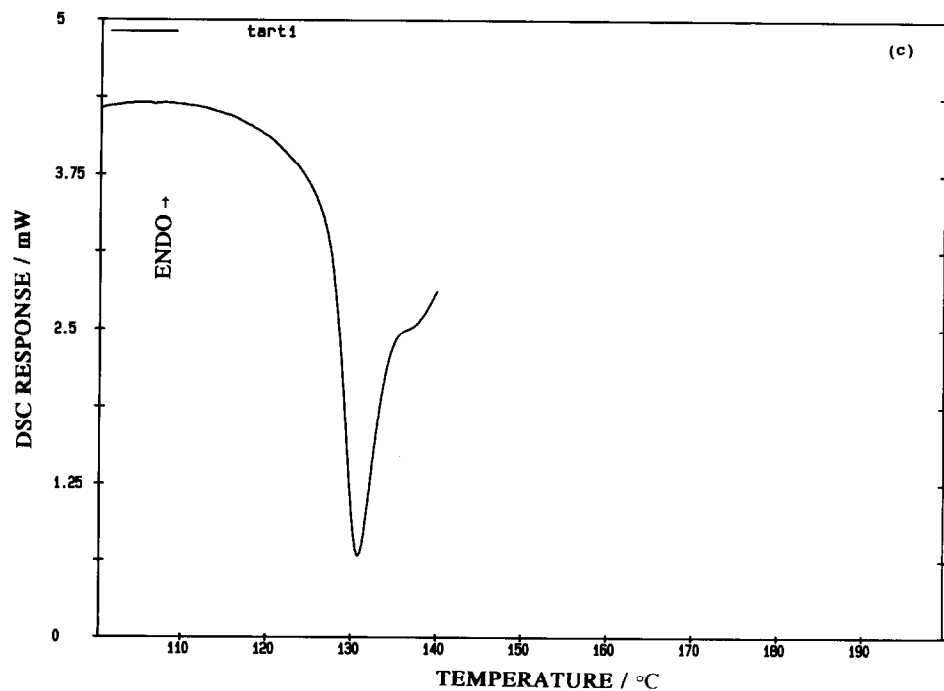
Fig. 1. (a), (b)

Fig. 1. (c), (d)

Table 2
Effect of heating rate and sample size on the exothermic reaction

Sample	Mass/mg	Heating rate/($^\circ$C min^{-1})	Ignition
$K_2[MoO(O_2)_2(tart)] \cdot 2H_2O$ (Tart 1)	1.472	5	No
	1.241	10	Yes
	1.436	20	Yes
	4.282	20	Yes
$K_2[Mo_2O_2(O_2)_4(tart)] \cdot 4H_2O$ (Tart 2)	0.633	10	No
	1.055	10	Yes
	3.559	20	Yes
$K_2[Mo_2O_2(O_2)_4(mal)] \cdot 2H_2O$ (Mal)	0.316	5	No
	0.514	10	No
	0.973	10	No
	1.500	10	Yes
	1.326	20	Yes
$K_2[Mo_2O_2(O_2)_4(gly)] \cdot 2H_2O$ (Gly)	0.243	5	No
	0.450	10	Yes
	0.235	20	Yes
	1.327	20	Yes

$K_2[MoO(O_2)_2(tart)] \cdot 2H_2O$ (Tart 1) and $K_2[Mo_2O_2(O_2)_4(tart)] \cdot 4H_2O$ (Tart 2)

Although chemical analysis and spectroscopy both indicate differences in these two complexes, their thermal behaviour, at least in the first very exothermic reaction, is very similar. The TG curves for the two tartrate complexes, Tart 1 (4.282 mg) and Tart 2 (3.559 mg), heated at 20.0°C min^{-1} in N_2 are shown in Fig. 1(a). The onset temperatures for the rapid mass loss are virtually identical at 133 ± 1°C. The differences in the percentage mass losses probably arise from ejection of material from the sample pan during the rapid reaction. At a slower heating rate (5.0°C min^{-1}) the TG curve for Tart 1 (Fig. 1(b)) shows several stages and the onset of the first major stage is at about 124°C and there is a rate maximum at 128°C.

The DSC curve for a 0.470 mg sample of Tart 1 heated at 20.0°C min^{-1} in N_2 (Fig. 1(c)) shows onset of a strong exotherm at about 125°C. Larger sample masses, when heated under similar conditions, gave sharper exotherms, as illustrated for 2.890 mg of Tart 2 in Fig. 1(d), where the onset temperature is 127°C.

$K_2[Mo_2O_2(O_2)_4(mal)] \cdot 2H_2O$ (Mal)

The DSC curve for the malonate complex Mal (1.530 mg heated at 20.0°C min^{-1} in N_2) is shown in Fig. 2(a). The onset of the exotherm is at 193°C.

Fig. 1. (a) TG curves for the two tartrate complexes, Tart 1 (4.282 mg) and Tart 2 (3.559 mg), heated at 20.0°C min^{-1} in N_2. (b) The TG and DTG curves for Tart 1 (1.472 mg) heated at 5.0°C min^{-1} in N_2. (c) The DSC curve for a 0.470 mg sample of Tart 1 heated at 20.0°C min^{-1} in N_2. (d) The DSC curve for a 2.890 mg sample of Tart 2 heated at 20.0°C min^{-1} in N_2.
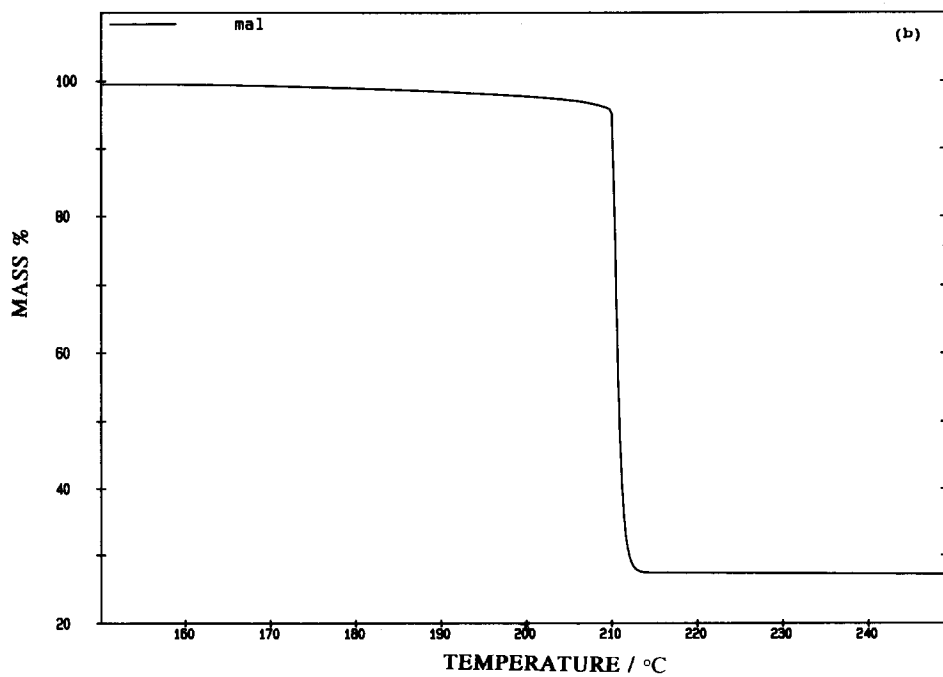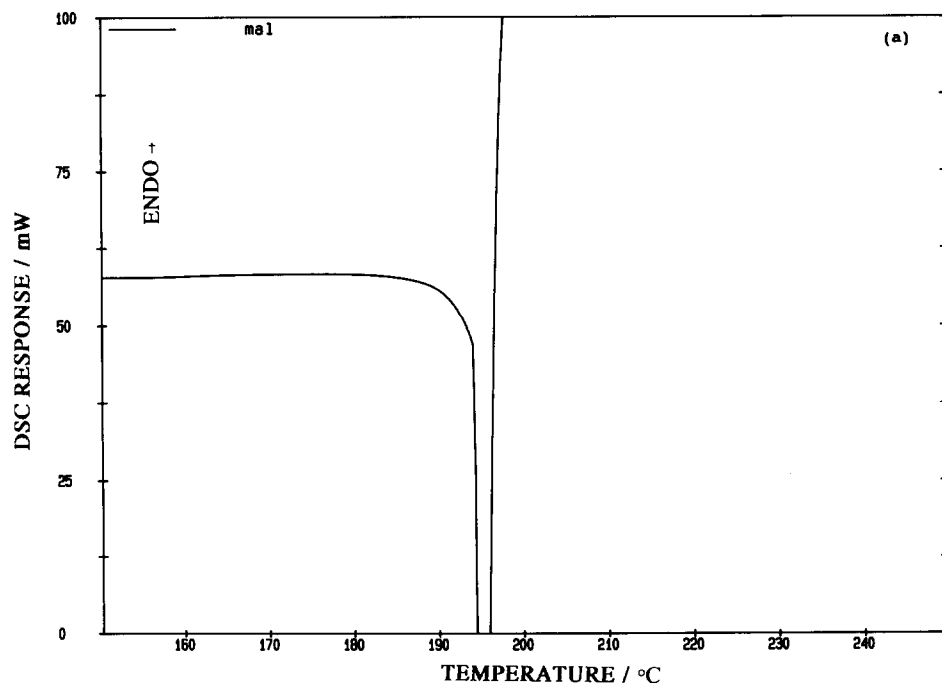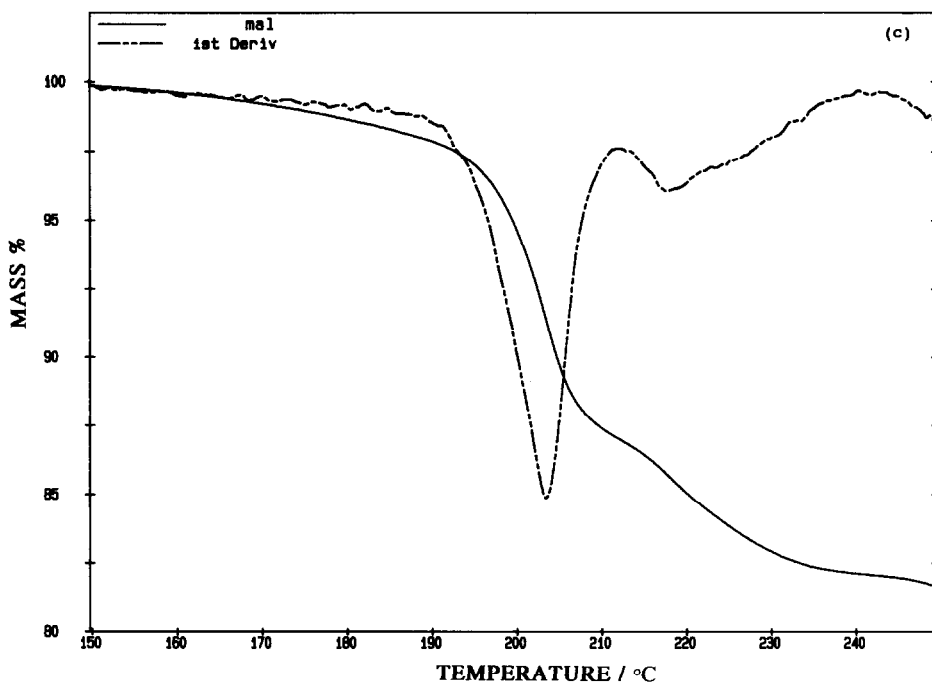
Fig. 2. (a), (b)

Fig. 2. (a) The DSC curve for the malonate complex Mal (1.530 mg) heated at 20.0°C min⁻¹ in N₂. (b) The TG curve for Mal (1.326 mg) heated at 20.0°C min⁻¹ in N₂. (c) The TG and DTG curves for Mal (0.973 mg) heated at 10.0°C min⁻¹ in N₂.

A TG curve (1.326 mg heated at 20.0°C min⁻¹ in N₂) for the same complex is shown in Fig. 2(b). The onset of the explosive mass loss is at 210°C. When the sample mass and the heating rate were decreased to 0.973 mg and 10.0°C min⁻¹, respectively, the resulting TG and DTG curves are shown in Fig. 2(c). The decomposition is slower and involves several stages. The onset of the first stage is at 191°C and the maximum rate occurs at 203°C.

$K_2[Mo_2O_2(O_2)_4(gly)] \cdot 2H_2O$ (Gly)
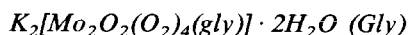
The overall behaviour of the glycine complex Gly parallels that described above for the malonate and tartrate complexes except for differences in the onset temperatures. The DSC curve for a 1.280 mg sample heated at 20.0°C min⁻¹ in N₂ is shown in Fig. 3(a). The onset of the exotherm is at 163°C. The TG curve (1.327 mg heated at 20.0C min⁻¹ in N₂) is shown in Fig. 3(b). The onset of the rapid mass loss is at 172°C.

Under non-ignition conditions, the TG curve (0.243 mg heated at 5.0°C min⁻¹ in N₂), shown in Fig. 3(c), has the onset of the first major stage of decomposition at 157°C and the maximum rate at 176°C.
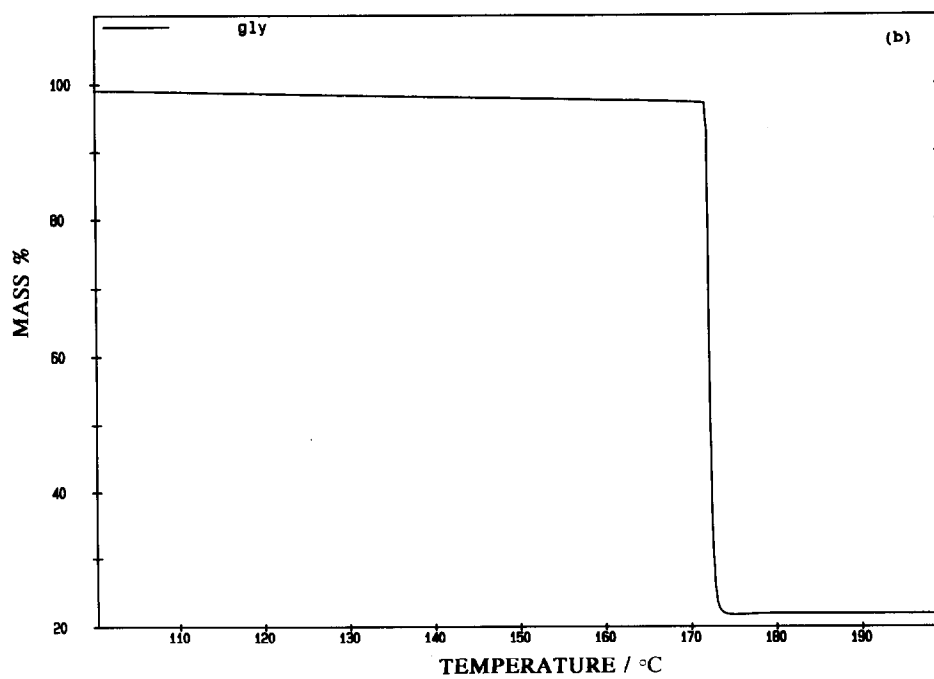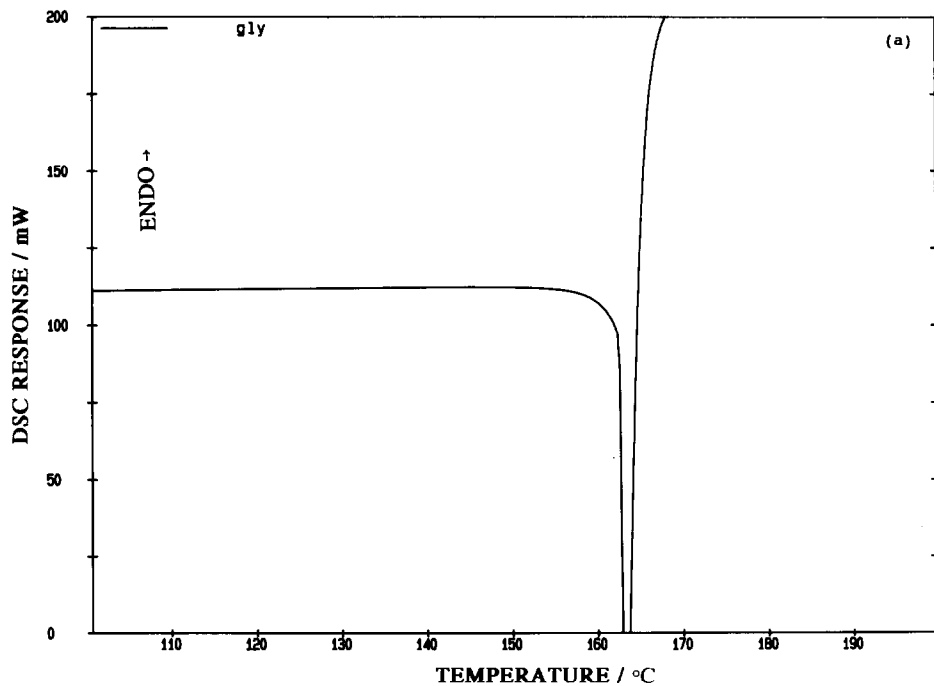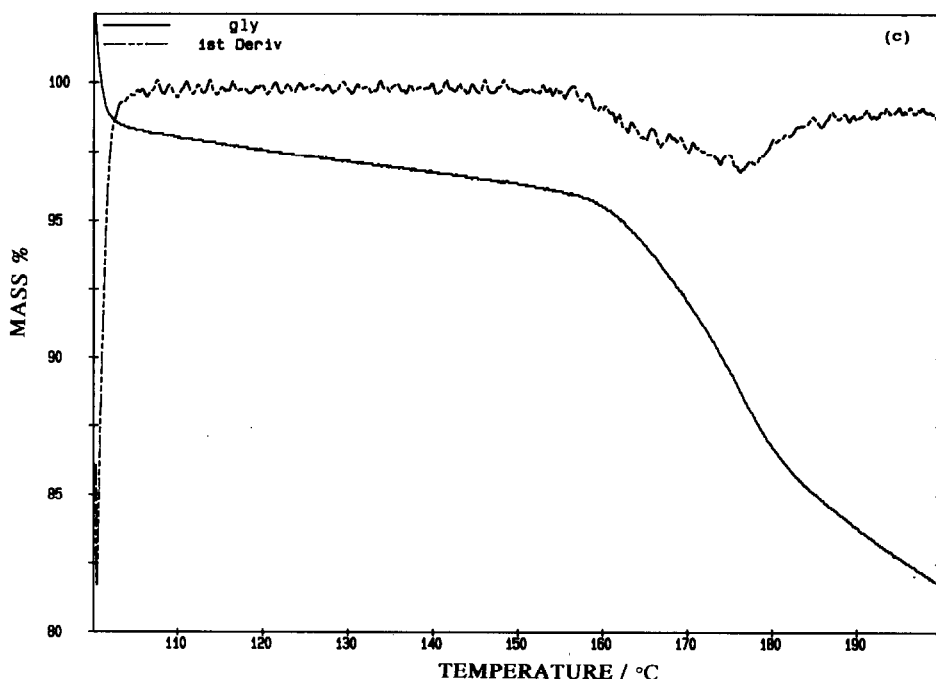
Fig. 3. (a), (b)

Fig. 3. (a) The DSC curve for a 1.280 mg sample of the glycine complex Gly heated at 20.0°C min^{-1} in N$_2$. (b) The TG curve for Gly (1.327 mg) heated at 20.0°C min^{-1} in N$_2$. (c) The TG and DTG curves for Gly (0.243 mg) heated at 5.0°C min^{-1} in N$_2$.

Table 3
Onset temperatures (°C) for the exothermic reaction measured in the TG and in the DSC

Sample	DSC onset	TG onset	Max	ΔT [a]
K$_2$[MoO(O$_2$)$_2$(tart)] · 2H$_2$O and	127	133		+6
K$_2$[Mo$_2$O$_2$(O$_2$)$_4$(tart)] · 4H$_2$O		124	128	
K$_2$[Mo$_2$O$_2$(O$_2$)$_4$(gly)] · 2H$_2$O	163	172		+9
		157	176	
K$_2$[Mo$_2$O$_2$(O$_2$)$_4$(mal)] · 2H$_2$O	193	210		+17
		191	203	

[a] $\Delta T = TG_{onset} - DSC_{onset}$.

Results are summarised in Table 3. It can be seen that, if the assumptions made are justified, i.e. that the DSC is accurately calibrated and that the onset temperatures measured in the two instruments can be expected to be the same, the calibration of the TG is in error over this temperature range and that the deviation from the true value is not a constant temperature difference, but increases with temperature.

4. Conclusions

The use of the explosive decomposition of small samples of highly energetic materials shows potential for calibration of TG systems relative to DSC systems calibrated by more conventional means. The sharpness of the mass loss gives a more defined temperature than the Curie transitions. The molybdenum-peroxo complexes suggested are only a few examples of materials which are reasonably safe to handle, are stable on careful storage and yet provide suitably exothermic decompositions. Many other compounds will undoubtedly prove similarly useful (or even superior) for calibration using the principle suggested.

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