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Note

Differential scanning calorimetric studies of decomposition of β-lead azide

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Lead azide is one of the most extensively used primary explosives in industrial and military applications. However, "spontaneous" explosions in this material make it hazardous. It has been suggested[1] that one of the four crystalline forms of this material, namely the β-form, is responsible for causing spontaneous explosions. Locked-in strains during the growth of the crystals were thought to lead to crystal fracture and the initiation of explosion. However, there is now considerable experimental evidence that fracture in the crystal alone does not cause initiation of reaction. In high speed photographic studies[2, 3] it has been shown that even very extensive and violent fracture does not cause fast decomposition. For a full understanding of the explosive properties of lead azide it is clearly important to know the decomposition parameters of the various crystal forms to reasonable accuracy.

There has been extensive investigation of the more commonly used α-form, but very little work on the decomposition parameters of the β-form. The only reported work is that of Garner and Gomm[4] in 1931 who found that the activation energy for decomposition is 38.8 kcal mole^{-1}. We describe here a differential scanning calorimetric study of the decomposition of β-lead azide. The activation energy was found to be in good agreement with that found by Garner and Gomm[4], but the pre-exponential factor is several orders of magnitude smaller. A similar study for tetracene has been described by us elsewhere[5] and this gives fuller details of the experimental techniques used.

EXPERIMENTAL

β-lead azide single crystals were grown in the laboratory using a diffusion method. The crystals obtained were long thin ribbons from which geometrically "good" quality ones were selected. The thermal decomposition studies were made using a Perkin–Elmer differential scanning calorimeter, model DSC-2. The temperature calibration of the instrument was carried out at the melting points of indium (m.p. 429.8 K) and lead (m.p. 600.7 K).

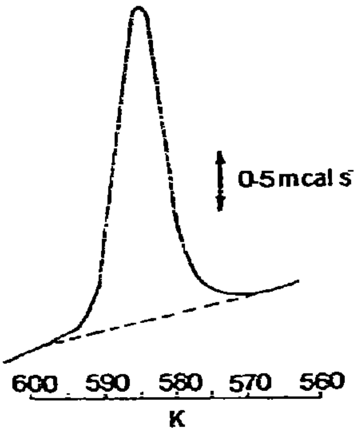

Fig. 1. A typical DSC trace for β-lead azide obtained with a heating rate 0.33 K s^{-1}.

For a typical DSC run the sample consisted of 3–8 β-lead azide crystals each of size ~ 5 mm × 200 μm × 30 μm and with the total weight of crystals being 0.2–1.0 mg. The sample was placed in an aluminium foil pan and then covered with an aluminium lid. The purge gas was argon at a pressure of 168 k Pa; the temperature of the pan was increased at a pre-selected rate. As Fig. 1 shows the DSC trace of this material has only one peak (some exothermic materials e.g. tetracene[5] and lead azotetrazole[6] produced DSC traces with more than one peak). DSC traces were obtained for various heating rates in the range 0.021–0.667 K s^{-1} (1.25–40.0 K min^{-1}) from which peak temperatures were measured.

RESULTS

It was found that the peak temperature of the trace increased with the rate of heating. This observation is in agreement with those of many workers[5, 7, 8] and can be used to derive decomposition parameters using the methods of Kissinger[9] and Ozawa[8, 9] which are briefly described below.

(A) *Kissinger method*

It was shown by Murray and White[7] that for a first order chemical reaction

$$Ae^{-E/RT_m} = \frac{E}{RT_m 2} \frac{dT}{dt} \tag{1}$$

where R is the gas constant, T the absolute temperature, dT/dt the heating rate, T_m the peak temperature, E the activation energy for decomposition and A the pre-exponential factor. Equation (1) can be written as

$$\ln(\phi/T_m^2) = \ln\left(\frac{RA}{E}\right) - \frac{E}{RT_m} \tag{2}$$

where

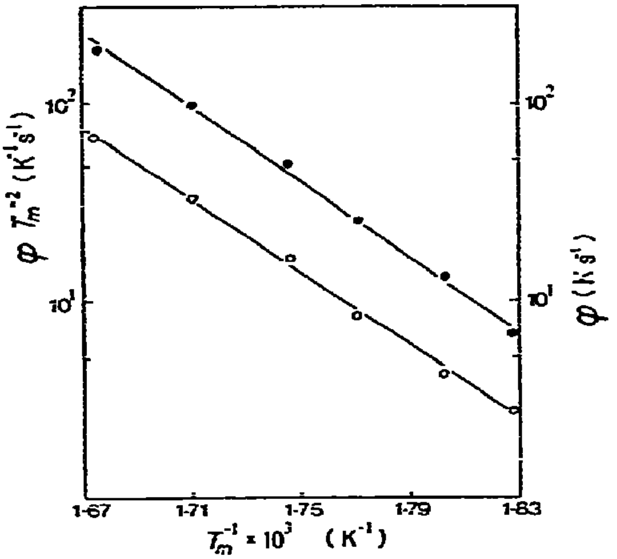

Fig. 2. Plots ϕT_m^{-2} vs. T_m^{-1}–0 (Kissinger Method) and ϕ vs. T_m^{-1}–0 (Ozawa Method).

$$\phi = \frac{\mathrm{d}T}{\mathrm{d}t}$$

Kissinger[9] plotted $\ln(\phi/T_m^2)$ vs $1/T_m$ for a number of materials and obtained straight lines from which he calculated the activation energies of the reactions.

In a subsequent paper Kissinger[10] showed that eqn. (2) holds for an n^{th} order reaction as well.

A plot of $\ln(\phi/T_m^2)$ vs $1/T_m$ for β-lead azide is shown in Fig. 2. It will be seen that it is a good straight line. The value of the activation energy obtained is 39 ± 2 kcal mole^{-1}. The pre-exponential factor is $9.7 \pm 0.4 \times 10^{12}$ s^{-1}. This value is ~ 10^7 times smaller than the value reported by Garner and Gomm for slow decomposition, though it agrees well with the value of 1.2×10^{13} s^{-1} for detonation[11].

(B) *Ozawa method*

A different method for obtaining the kinetic parameters from thermograms has been developed Ozawa[8]. Ozawa's analysis shows that for a generalized chemical reaction $1/T_m$ varies linearly with $\ln(\phi)$, and the slope of the line is $-0.456\ E/R$. Krien[6] has successfully used this approach for analysing the DSC data for lead azotetrazole.

Figure 2 shows that a plot of $\ln(\phi)$ vs $1/T_m$ is a straight line. The activation energy obtained from this line is 40 ± 1.5 kcal mole^{-1}, which is in good agreement with that calculated by the Kissinger method.

DISCUSSION

This investigation has shown that differential scanning calorimetry can be

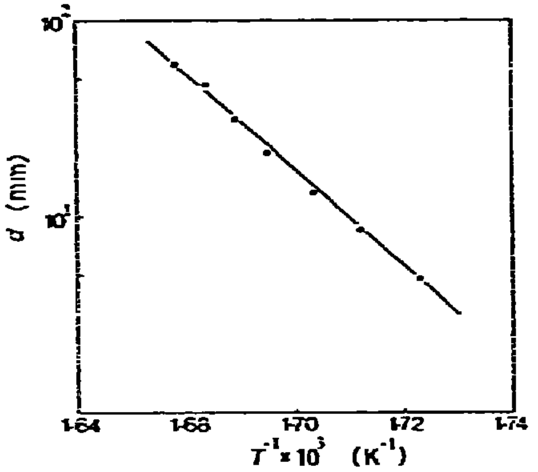

Fig. 3. Plot of ln d vs. T^{-1} (Roger and Morris Method).

successfully used for decomposition studies of β-lead azide. It is only recently that workers have applied DSC techniques to studies of explosive materials. Previously, most of the thermal decomposition studies of explosives were made isothermally, the rate of reaction being followed by monitoring the rate of evolution of gaseous products of the decomposition[12, 13]. In our DSC studies the sample temperature increases with time and the agreement of the activation energy for decomposition found by this technique with that found by Garner and Gomm[4] suggests that the two different techniques can yield similar results. It is also possible to make successful isothermal decomposition studies with the DSC, as has been shown in recent work on tetracene[5].

Besides the Kissinger and Ozawa methods of analysis, another method, due to Roger and Morris[14], has also been employed by some workers. In this approach activation energy is derived from a DSC trace, using the relationship

$$-E = R\frac{\ln d_1 - \ln d_2}{1/T_1 - 1/T_2} \tag{3}$$

where d_1 and d_2 are the distances between the points on the curve and the baseline corresponding to temperatures T_1 and T_2 respectively. We have made plots of ln d vs $1/T$ as shown in Fig. 3 and found that the activation energy for decomposition is 110 ± 6 kcal mole^{-1} which is a factor of ~ 3 greater than that found by the Kissinger and Ozawa methods. However, the Roger and Morris method is only applicable to reactions which are governed by an equation $d\alpha/dt = k$, where α is the fractional decomposition at time t, and k is the rate constant (i.e. $Ae^{-E/RT}$). For a reaction obeying $\alpha = kt^n$ where $n > 1$, eqn. (3) will not apply.

Our values of the activation energy for decomposition of β-lead azide is higher than that for α-lead azide (30 kcal mole^{-1}) reported by Fox[15] and slightly less than that found by Garner and Gomm for α-lead azide (47.7 kcal mole^{-1}). This combined with the fact that fracture of lead azide does not initiate an explosive reaction suggests that explosions during the crystallization of lead azide from solutions is more likely to be due to the electrical discharges between layers of crystals[16, 17].

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