Study of the Thermal Decomposition of Pentaerythritol Tetranitrate

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The thermal decomposition of pentaerythritol tetranitrate (PETN) has been studied below its m.p. 141 °C. Both sublimation and decomposition are found to occur concurrently. Decomposition begins at *ca.* 75 °C and pressure–time curves show an initial rapid acceleration in decomposition. An activation energy of 192 ± 5 kJ mol^{-1} is obtained between 75 and 130 °C. It is suggested that decomposition takes place in the vapour phase. Mass spectra of the decomposition products show that the distribution is temperature dependent.

PENTAERYTHRITOL TETRANITRATE (PETN) is a widely used secondary explosive. Its relatively high chemical stability allows it to be manufactured, handled, and stored with comparative safety. Andreev and Kaidymov [1] have studied the thermal decomposition of PETN and found that the vapour phase is the least stable. They also showed that the decomposition is greatly affected by the presence of water vapour and slightly by the presence of oxygen. Their value for the activation energy, E, for the decomposition of solid PETN lay between 215 and 263 kJ mol^{-1} but was based on a limited amount of data. Values from other workers, found using a variety of methods, fall reasonably closely together. Rogers and Morris [2] using the differential scanning calorimetry technique found a value for E of 198 kJ mol^{-1}. Soria-Ruiz [3] obtained 176 kJ mol^{-1} by monitoring the peak m/e 28 using a quadrupole mass spectrometer. Vapour phase decomposition was studied by Robertson [4] who found E 197 kJ mol^{-1}. Maycock and Verneker [5] used thermobarogravimetric techniques and obtained 188 kJ mol^{-1}. Most workers agree that the decomposition is complex and takes place concurrently with sublimation. Decomposition products at 210 °C were analysed chemically by Rideal and Robertson [6] who found that the products in a closed system were given by equation (1).

$$\begin{aligned}C_5H_8N_4O_{12} = {} & 0.52NO_2 + 2.11NO + 0.42N_2O + \\ & 0.28CO_2 + 0.93CO + 0.09H_2 + \\ & \text{water} + \text{formaldehyde} + \text{residue} \qquad (1)\end{aligned}$$

The present work was undertaken to reinvestigate the decomposition but this time using an ultra high vacuum system and analysing the products using a time-of-flight mass spectrometer.

EXPERIMENTAL

PETN in powder form was obtained from E.R.D.E., Waltham Abbey. It was then recrystallized twice from acetone solution by slow evaporation. The resulting crystals were white, transparent, and exhibited semi-regular hexagonal shape. Large single crystals of up to *ca.* 3 × 5 × 20 mm in size were obtained by this method. Cleavage planes were found to be parallel to the hexagonal faces. Small crystals of *ca.* 0.2 mg were cleaved from the as-grown crystal. Only freshly cleaved material was used for the decomposition study.

A six-way stainless steel reaction chamber had one end attached to a conventional ultra high vacuum system and the other connected to the flight tube of a Bendix RGA-1A time-of-flight mass spectrometer. The ion source was *ca.* 40 mm away from the site where reaction took place. A small furnace had a glass reaction vessel (5 mm outside diameter) situated vertically along its axis. A Pt–(Pt, 13% Rh) thermocouple was in contact with the bottom of the reaction vessel. Temperatures of up to *ca.* 300 °C with an accuracy of ±0.5 °C could be achieved. The PETN crystals were kept in a stainless steel tray, *ca.* 140 mm above the reaction vessel, during the system bake-out at 150 °C. The section containing the sample was not baked and was kept below 40 °C. A linear motion drive was used to introduce the sample into the reaction vessel. The crystal thus only entered the reaction vessel when the conditions for an experiment were favourable.

The furnace was outgassed at 300 °C with the system baked-out overnight. The final operating vacuum was 1×10^{-8}—1×10^{-7} Torr. A glass window in front of the reaction chamber enabled a direct view of the specimen while the reaction was carried out.

In the isothermal decomposition experiment, the total pressure measured by the ion gauge was displayed on a Varian chart recorder, model G14. For other experiments the specimen was heated from room temperature at a rate of 20° min^{-1} by manually increasing the furnace current. From the pressure values the rate of increase in pressure at various temperatures was obtained. In order to analyse the decomposition products, the valve leading to the ion pump was adjusted so that the total pressure in the system during maximum decomposition was maintained within the pressure range 10^{-6}—10^{-5} Torr. The spectrum was taken at 70 eV from a display on a Tektronix oscilloscope model 7603 using a polaroid camera model C27.

RESULTS

The thermal decomposition of PETN was studied below its m.p., 141 °C. Isothermal pressure–time curves taken at 80, 88, and 110 °C are shown in Figure 1. At each temperature the pressure rises rapidly in the initial stage and then decelerates; in the case of curve C the pressure increases again after *ca.* 90 min. The pressure–time curve taken at 53 °C is shown in Figure 2. (Note the increased vertical scale of this figure compared with that of Figure 1.) At this temperature, there is an initial linear region before the rate decreases. The final pressure is 1.3×10^{-6} Torr and is in reasonable agreement with the vapour pressure at the temperature of sublimation as determined by Crimmins.[7]

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Figure 3 shows an Arrhenius plot of the rate against temperature when the specimen was subjected to a linear heating rate of 20° min^{-1}. Two runs A and B were taken by heating up from room temperature and 65 °C respectively. An activation energy of 192 ± 5 kJ mol^{-1} can thus be deduced for run A between 75 and 130 °C. Run B runs parallel to the least squares line of run A. Below 75 °C the gas evolution rate is approximately constant. At the completion of the reaction, no solid residue was left. It was not possible to detect by visual observation whether surface melting took place during the reaction. However, it was observed that the originally transparent sample, when in the reaction vessel, gradually became opaque at its surface as the reaction progressed.

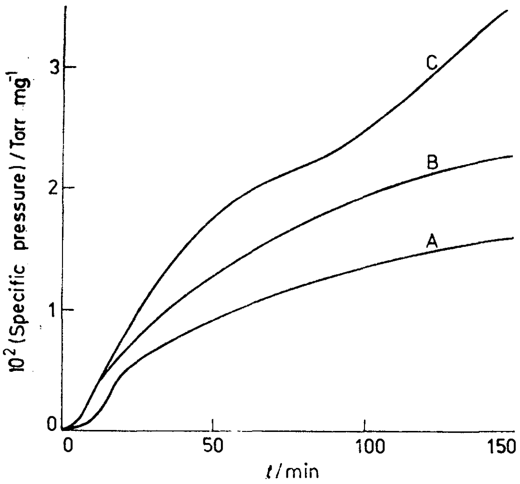

Figure 1 Pressure–time curves for isothermal decomposition where specific pressure is the value at time *t* per unit mass of PETN originally present: A, 80; B, 88; C, 110 °C

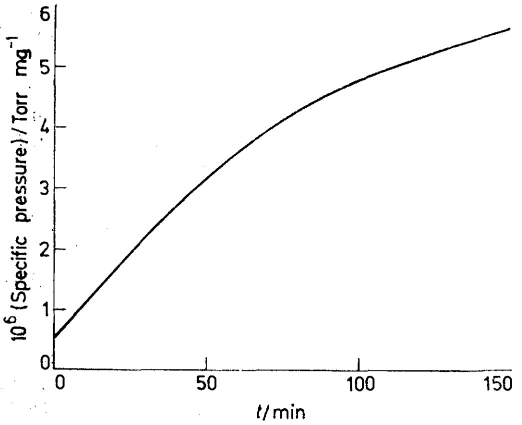

Figure 2 Specific pressure against time; decomposition temperature at 53 °C

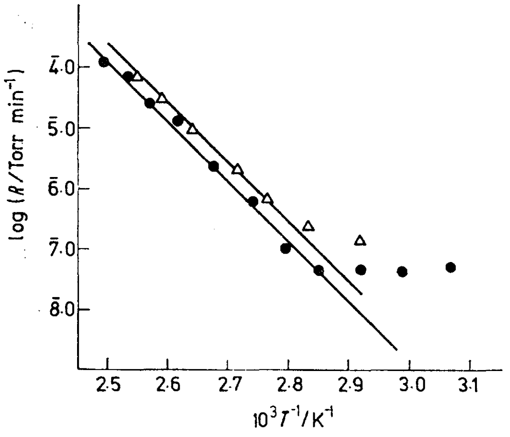

Figure 3 Arrhenius plot of the rate of gas evolution: ● heating up from room temperature (run A); △ heating up from 65 °C (run B)

Mass spectra were taken at 94, 126, and 158 °C [results are given in Supplementary Publication No. SUP 21684 (3 pp.)*]. The mass spectrum of the decomposition products has major peaks in the low mass region below *m*/*e* 50. Prominent peaks are *m*/*e* 18, 28, 29, 30, 44, and 46. The distribution is influenced by the temperature of decomposition. Below the m.p. of PETN (141 °C) a large amount of a peak with *m*/*e* 30 is found whereas at higher temperature *m*/*e* 18 and 28 dominate. These peaks correspond to the decomposition products H_2O, N_2, CO, HCHO, NO, CO_2, N_2O, and NO_2. Because the crystal is recrystallized from acetone, signals from the trapped solvent also show up in some of the spectra. The base peak occurs at *m*/*e* 43 due to the fragment ion CH_3CO^+, but the amount is not significant by comparison with the decomposition products. Over the high mass region (*i.e.* *m*/*e* > 50) prominent peaks occur at 55, 56, 76, and 85.

DISCUSSION

There has been some controversy regarding the thermal stability of solid PETN. Aubertein[8] recrystallized PETN twice from acetone and found that while untreated crystals of PETN gave an initial high loss of water and acid, recrystallized material did not decompose significantly when held at 100 °C for three weeks. However, Andreev and Kaidymov[1] using manometric methods, report detecting decomposition beginning at *ca.* 80 °C. Since atmospheric gases such as molecular oxygen and water vapour are known to affect the reaction rate the ideal situation is for the reaction to take place in an ultra high vacuum system. Our isothermal pressure–time curves show different types of behaviour depending on the temperature (Figures 1 and 2). Furthermore when a sample is heated up at a linear rate of 20° min^{-1} the rate of gas evolution increases exponentially above 75 °C. The mass spectrum taken above this temperature revealed large quantities of decomposition products together with some PETN vapour. The decomposition curves in Figures 1 and 2 have an initial rapid acceleration in rate which then gradually decreases. In the case of curve C (Figure 1), the highest temperature studied, the decrease is followed by a further increase. Levy[9] has found that NO_2 retards the decomposition of ethyl nitrate ($CH_3CH_2ONO_2$) while NO accelerates the reaction. These gases are produced in relatively large amounts here and it is possible that the way their relative abundance changes influences the decomposition of PETN.

* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue. Items less than 10 pp. are supplied as full-size copies.

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Several workers have studied the vapour pressure at different temperatures.[7,10,11] The calculated heat of sublimation ranges from 121 to 152 kJ mol^{-1}. The value of 121 kJ mol^{-1} obtained by Crimmins appears to be the most reliable since measurements were taken at a lower temperature range where decomposition is not significant. Recently Maycock and Verneker[5] have studied the kinetics of sublimation by weight loss measurements under a stream of helium gas maintained at a pressure of 5 × 10^{-2} Torr and found an activation energy of 109 kJ mol^{-1}. The absence of an exotherm in their differential thermal analysis data and the presence of decomposition products found by us strongly suggest that decomposition is preceded by sublimation and that it occurs predominantly in the vapour phase.

For mononitrate and nitrite esters, the primary process involves the rupture of the RO–NO_2 bond producing NO_2 or NO. The bond dissociation energy was estimated by Levy[9] to be *ca.* 173 kJ mol^{-1}. Our calculated activation energy of 192 kJ mol^{-1} for PETN is close to this and so from the energetic point of view, the primary process in the decomposition of PETN appears to be the rupture of one RO–NO_2 bond followed by the elimination of a neutral formaldehyde molecule [reactions (1) and (2)]. The relatively large amount of $CH_2O\ NO_2^+$ (*m/e* 76) present in the mass spectrum then suggests the ultimate break down of $C(CH_2ONO_2)_3$ as in reaction (3).

$$C(CH_2ONO_2)_4 \longrightarrow C(CH_2ONO_2)_3\,CH_2O + NO_2 \qquad (1)$$

$$C(CH_2ONO_2)_3\,CH_2O \longrightarrow C(CH_2ONO_2)_3 + HCHO \qquad (2)$$

$$C(CH_2ONO_2)_3 \longrightarrow 2\,CH_3ONO_2 + 2\,CO + NO \qquad (3)$$

Methyl nitrate, by analogy with the decomposition of $CH_3CH_2ONO_2$ (see, for example, ref. 12) could then undergo steps (4)—(9). These steps are all consistent with our

$$CH_3ONO_2 \longrightarrow CH_3O + NO_2 \qquad (4)$$

$$CH_3O + NO_2 \longrightarrow HCHO + HONO \qquad (5)$$

$$2\,HONO \longrightarrow H_2O + NO + NO_2 \qquad (6)$$

$$CH_3O + HCHO \longrightarrow CH_3OH + HCO \qquad (7)$$

$$HCO + NO \longrightarrow CO + HNO \qquad (8)$$

$$2\,HNO \longrightarrow H_2O + N_2O \qquad (9)$$

mass spectral results, and the reaction pattern established by Levy[9] for ethyl nitrate.

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