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CHARACTERIZATION OF THERMAL AND PHOTOSUBLIMATION OF ORGANIC EXPLOSIVES BY THERMOBAROGRAVIMETRIC TECHNIQUES

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ABSTRACT

The thermal and photosublimation of the three organic explosives pentaerythritol tetranitrate (PETN), 1,3,5-trinitro-1,3,5,-triazacyclohexane (RDX), and trinitrotoluene (TNT) have been studied as a function of the overpressure of an inert gas. Both of these phenomena appear to be quite efficient and similar to each other only in that they are both surface effects. The activation energy for photosublimation is always less than that for the thermally induced process. For the photon induced sublimation it has been found to be a one photon process where the photon energy necessary to cause sublimation need not be of sufficient energy to cause electronic transitions. A tentative model based on vibrational excitations, has been proposed for the photon induced process. For the thermal sublimation process it has been found that the activation energy for sublimation is very close to the previously known values for the enthalpy of sublimation.

INTRODUCTION

An understanding of explosion mechanisms necessitates identification of the rate determining step in the pre-detonation phenomena. This is a difficult task and often the slow thermal decomposition has been considered as the rate determining step for inorganic explosives. Rates of thermal decomposition have been successfully correlated to explosion parameters for some non-sublimable solids^1. With the sublimable explosives (usually organic solids) it is not apparent whether sublimation precedes decomposition or whether the two function simultaneously. For these same materials a requisite for pre-detonation characterization is that both sublimation and decomposition processes be characterized. A further complicating factor of some organic explosives is that they melt before explosion. Vapor pressure data and kinetics of this process are therefore relevant to the total predetonation characterization. It is also apparent that some of the organic explosives, *e.g.* 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) are quite sensitive to electromagnetic radiation^2. These earlier studies have also shown that these same explosives may exhibit photosublimation phenomena simultaneously with photochemical decomposition.

The determination of kinetic data for two processes functioning simultaneously is difficult and often introduces gross assumptions in interpreting the data. Maycock and Pai Verneker have perfected a thermobarogravimetric (TBGA) technique which is capable of explicitly determining sublimation and thermal or photochemical decomposition kinetics simultaneously for the same sample. This technique has already been applied to nitronium perchlorate[3].

The present work, utilizing primarily the TBGA technique, was accomplished to determine the kinetics and mechanisms of thermal and photosublimation processes found in the pre-detonation phenomena of the three organic secondary explosives PETN (pentaerythritol tetranitrate), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane) and TNT (trinitrotoluene).

EXPERIMENTAL

The apparatus and experimental technique used in this study have been described earlier[3]. The TBGA technique applies to a system where simultaneous measurements of the decomposition gas pressure and total sample weight loss can be made. The second important process to be well characterized is the stoichiometry of the decomposition process, for then the decomposition gas pressure can be translated into a weight loss if the volume of the system is also known. In the present work a residual gas analyzer was also coupled to the TBGA system to allow a more thorough analysis of the existence of normal decomposition and also an analysis of the products of decomposition.

For the photosublimation studies a low pressure Hg arc (Hanovia lamp) was mounted directly above the sample and being separated from it by the quartz furnace wall. For comparative rates as a function of temperature the radiant energy falling on the sample was maintained constant and the sample temperature varied by the programable Mettler furnace. To determine the relationship between the photosublimation and photon intensity, the intensity was varied by placing calibrated neutral density filters between the lamp and the sample.

The explosives used in this study were all of high purity grade, established by both differential thermal analysis and melting-point determination.

RESULTS AND DISCUSSION

Thermal sublimation

Most of the organic explosives have a relatively low melting point requiring that the TBGA runs be carried out with different inert gas overpressures. This allows differentiation between sublimation and decomposition for the solid, and evaporation and decomposition for the liquid (melt). Fig. 1 shows the differential thermal analysis (DTA) traces for PETN at 745 torr, 10 torr, and 10^{-2} torr. To simplify the figure the decomposition gas-pressure traces have not been included. At 745 torr, PETN exhibits a sharp melting point, followed by a decomposition exotherm. The absence of sublimation was determined visually, also by the non-existence of a sublimation endotherm

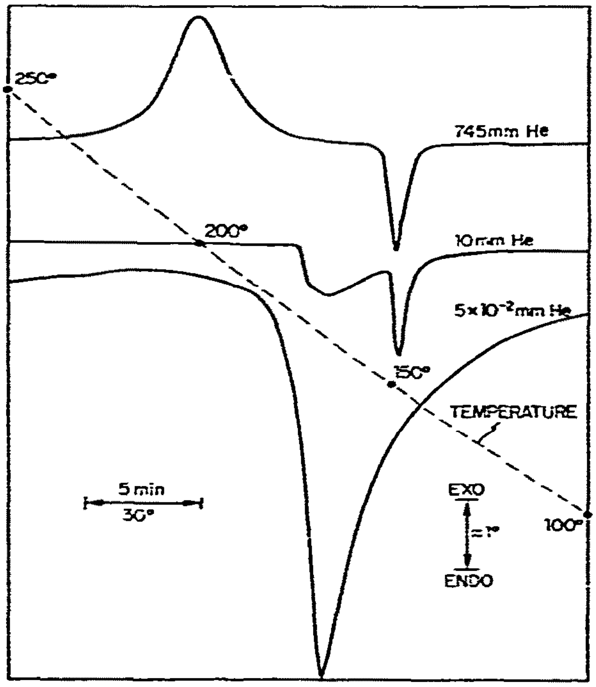

Fig. 1. Differential thermal analysis traces of PETN under different pressures of O_2- and H_2O-free He. A heating rate of 6°/min was used.

and by the good agreement between the calculated decomposition pressure and the experimentally observed pressure rise. In contrast, at 5×10^{-2} torr, there is no decomposition as evidenced by the mass spectrometer and resultant lack of pressure rise. The DTA shows a broad endotherm characteristic of sublimation. Although the DTA does not show a melting endotherm, PETN does indeed melt at 138 °C, observed visually, and by analysis of the TGA trace (shown later). At 10 torr the first endotherm represents the melting process. The endotherm has a long shoulder on the low temperature side representing sublimation. The melting endotherm is followed by a broad endotherm representing evaporation of the PETN melt. The pressure-time and thermogravimetric data at 10 torr indicate a sublimation and no decomposition process, again substantiated by mass spectrometric analysis where it was found that the decomposition species of PETN were absent.

Isothermal sublimation studies were performed with a 10-torr overpressure of dry, O_2- and H_2O-free He. For solid PETN the plot of α, the fractional sublimation *vs.* time gave a good straight line from 0 to 0.98 (shown in Fig. 2). This is reasonable based on the fact that PETN can be considered a monomolecular solid and its vapor is probably composed of monomolecular gaseous PETN species. With this model the concentration of the molecules in the surface sites from which sublimation proceeds should remain constant requiring that the sublimation rate should be constant as observed. These observations show that the sublimation process in PETN is similar to that of a monoatomic solid, *e.g.* most metals.

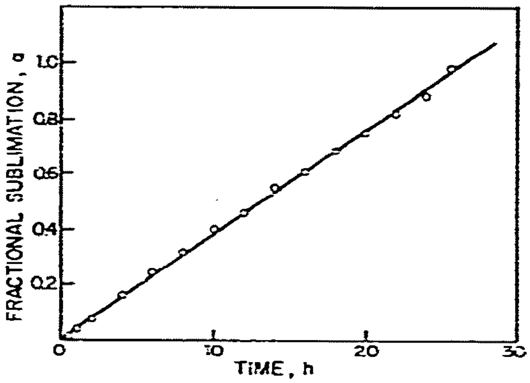

Fig. 2. Relationship between the fractional sublimation, α, and time for PETN, at 120°C.

By analogy with other monomolecular solids it is to be expected that the activation energy for sublimation (E) is approximately equal to the latent heat of sublimation (ΔH) since the entropy term is very small[4]. From these isothermal data an Arrhenius plot of the sublimation-rate constants gives an activation energy of 25.3 kcal.mole^{-1}. Similarly a plot of the logarithm of the time for fixed fractions of sublimation ($\alpha = 0.5$) against reciprocal temperature gave an activation energy of 26.7 kcal.mole^{-1}. This last method of analyzing the data is based on the well proven technique, independent of reaction kinetics, as applied to many thermal decomposition problems.

The analytical methods just presented are all for isothermal data which therefore involves the collection of a vast amount of experimental data. Since the experimental arrangement for generating thermogravimetric (TGA) data is extremely sensitive and controlled by an accurate and reproducible temperature programmer we have attempted to analyze single TGA traces in the hope of producing realistic sublimation parameters. If we let w be the apparent residual weight fraction from a TGA curve, then for kinetic processes in general

$$-\mathrm{d}w/\mathrm{d}t = k\,\mathrm{f}(w)$$

where k is an empirical rate constant, and $\mathrm{f}(w) = 1$ or w for zero order or first order processes respectively. It is also evident that

$$k = a \exp(-E/RT)$$

and that the complete kinetic equations for zero and first order processes are

$$-(\mathrm{d}w/\mathrm{d}t) = ka \exp(-E/RT)$$

and

$$-(\mathrm{d}w/\mathrm{d}t) = k\,aw \exp(-E/RT)$$

The TGA data has been analyzed by both of these analytical expressions and is clearly inconsistent with the isothermal data. However, an analysis based on plotting log (% weight lost) against the reciprocal temperature does give two reasonable straight lines with the "knee" occurring at the melting point of PETN, Fig. 3. The

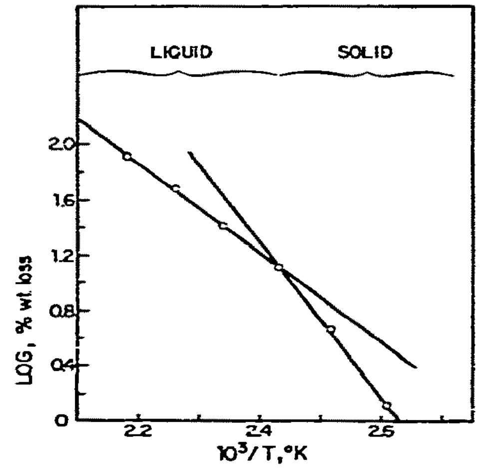

Fig. 3. Relationship between log (% wt. loss) and temperature for both liquid and solid PETN.

activation energy derived by this analysis, 26 kcal.mole^{-1} for the activation energy of sublimation, is in reasonable agreement with the isothermal value. This agreement may be fortuitous since we do not have any analytical model to explain the agreement. This method of analysis does, however, merit a theoretical investigation. Similarly an identical analysis of a decomposition TGA trace has been analyzed to give an activation energy of thermal decomposition of 45 kcal.mole^{-1} which is in good agreement with the value of 47 kcal.mole^{-1} found by Robertson[5] using isothermal constant volume techniques.

Similar experimental studies of the sublimation of TNT and RDX have been performed and analyzed by the techniques described for PETN. A compilation of the activation energies of sublimation for thes materials is given in Table I. In this table we have also compared our values with values of the molar heats of sublimation[5–7] since other values of the activation energies for sublimation for these organic explosives are not available.

TABLE I

ACTIVATION ENERGIES (KCAL. MOLE^{-1}) FOR SUBLIMATION AND EVAPORATION COMPARED TO OTHER TECHNIQUES

Analytical methods	*PETN*		*TNT*		*RDX*	
	Solid	*Melt*	*Solid*	*Melt*	*Solid*	*Melt*
$\alpha = kt$	25.3	—	29.9	—		
$\log 1/1-\alpha = kt$	—	17.0	—	19.1		
Time for $\alpha = 0.5$	26.7	—	31.2	18.0		
TGA, log (% wt loss)	26.0	14.7	31.3	16.1	26.2	16.1
Other work	—	—	30.0[5]	17.0[5]	26.8[6] 31.1[7]	—

In addition to analyzing the region of the TGA traces relevant to the solid, the region relative to the molten explosive was also analyzed. As pointed out earlier we are observing only the evaporation of the explosive and not its thermal decomposition. These data have been analyzed by the techniques described in detail for solid PETN and again the activation energies for evaporation of the melts are presented in Table I together with the appropriate values for the heats of evaporation. By inspection of this table it is apparent that these new techniques provide a method to determine, with a fair degree of accuracy, the activation energies of sublimation and evaporation which in turn are relatively close to the values for the enthalpy of sublimation, etc.

Photosublimation

Photosublimation for the three explosives, PETN, TNT, and RDX has been examined. In all cases photosublimation is observed at reduced pressures. For the case of PETN the pressure dependence of the photosublimation is shown in Fig. 4.

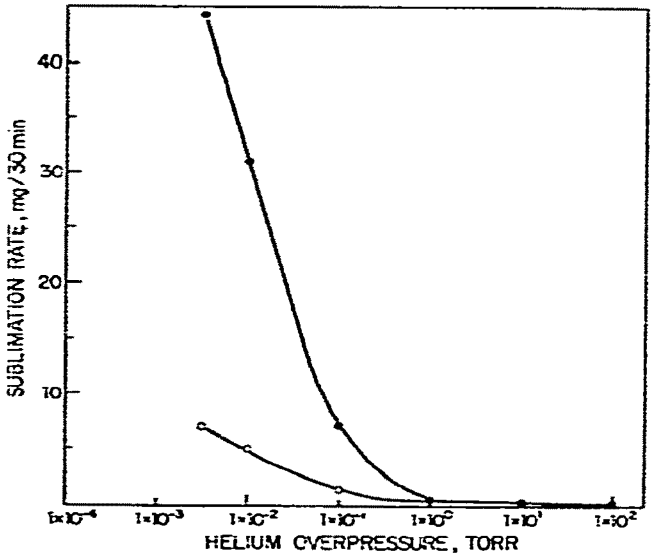

Fig. 4. Relationship between sublimation rate and overpressure of He at 77 °C for PETN; photosublimation (●) and thermal sublimation (○).

It is most apparent from this figure that at low temperatures photosublimation using a u.v. lamp is much more predominant than thermal sublimation, also shown in the figure. For all studies directed towards quantitative measurements the overpressure employed was 0.1 torr. RDX and TNT exhibited a similar behaviour in its pressure dependence. Similarly all three explosives have a photosublimation rate that is proportional to the intensity of the radiant energy (Fig. 5). The implication of these data is that the sublimation process is a one photon process which is to be expected. These pressure and rate–intensity data were all collected using the 2537Å line of the low pressure lamp which is well into the absorption bands of the parent explosives. However, it is possible that the light could induce decomposition nuclei on the surface to facilitate thermal sublimation. This possibility was examined by measuring the basic

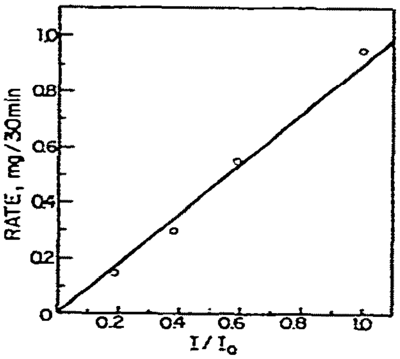

Fig. 5. Rate–intensity relationship for the photosublimation of PETN at 60 °C.

thermal sublimation rates before and after irradiation and were found to be identical. The photosublimation data have also been plotted as α (fractional sublimation) against time, resulting in good linear plots, to give a family of temperature dependent rate constants. When these were plotted in the form log k *vs.* $1/T$ they gave activation energies of 11.96, 12.0 and 20.7 kcal.mole^{-1} for PETN, TNT, and RDX respectively, as compared to the thermal activation energies of 26.0, 31.0, and 26.0 kcal.mole^{-1}. This change in activation energy with the photo being less than the thermal sublimation is a good indication that the phenomena being observed is in fact photosublimation. A comparison of the activation energy data for PETN is given in Fig. 6, where it should be noted that the data for the photosublimation are obtained by subtracting the thermal from the total sublimation data.

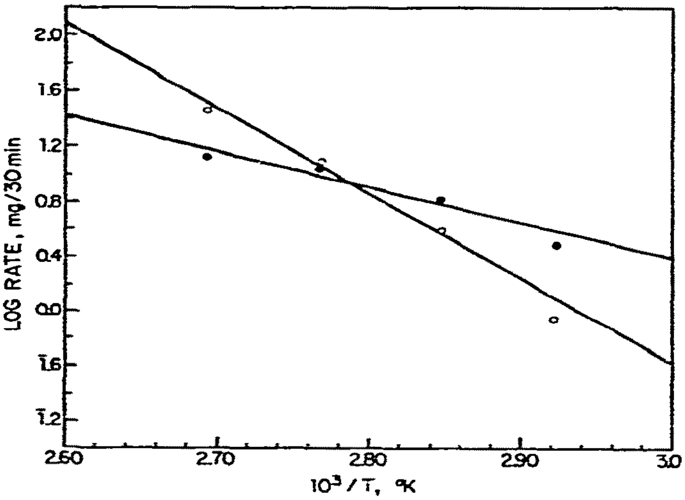

Fig. 6. Activation-energy plot for thermal sublimation (○) and photosublimation (●) of PETN.

By inspection of the rate values in Figs. 5 and 6, where for PETN 3 mg/30 min is equivalent to ~6×10^{15} mols/sec, it is apparent that the photosublimation is a surprisingly efficient process.

The rate of photosublimation as a function of wavelength has also been examined with the data for PETN being shown in Fig. 7 along with an indication of the

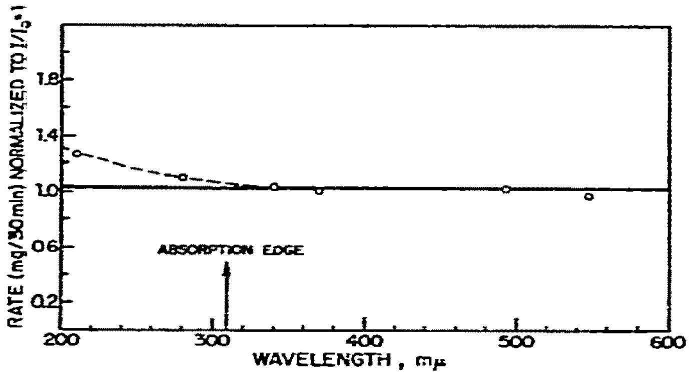

Fig. 7. Photosublimation rate-dependence on wavelength for PETN.

position of the absorption edge. RDX and TNT show a similar behavior. It is extremely clear from these data that at least up to 600 mμ the photosublimation rate is almost independent of the radiant wavelength. There is a slight increase in rate within the absorption edge which we believe to be real due to its reproducibility. An interpretation of these data is that electronic transitions are not necessarily required for the sublimation to proceed. A possible interpretation of this rate-wavelength behavior is that all of these energies are sufficient to produce vibrational transitions (excitations) in the molecules such that the Van der Waals forces holding the molecules together are perturbed such that photosublimation can occur.

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