

KINETIC STUDIES OF THE THERMAL DECOMPOSITION OF TETRYL USING ACCELERATING RATE CALORIMETRY. PART I. DERIVATION OF THE ACTIVATION ENERGY FOR DECOMPOSITION

PAULINE P. LEE

CANMET, Energy, Mines and Resources Canada, Ottawa, Ontario K1A 0G1 (Canada)

MARGARET H. BACK

Department of Chemistry, University of Ottawa, Ottawa, Ontario K1N 9B4 (Canada)

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ABSTRACT

The thermal decomposition of tetryl was studied in an accelerating rate calorimeter using spherical titanium and Hastelloy C bombs. Two decomposition peaks were observed. Three methods for the derivation of the activation energy for decomposition from the data were evaluated. The methods were in good agreement and gave values of 52 ± 1 kcal mol⁻¹ for the first peak and 43 ± 1 kcal mol⁻¹ for the second peak, for the decomposition in the Hastelloy C bomb. The values obtained from the decomposition in the titanium bomb were about 3 kcal mol⁻¹ lower. Activation energies measured by techniques using increasing temperature are compared with those measured isothermally and reasons for the differences are discussed.

INTRODUCTION

An understanding of the potential thermal hazards of explosives is imperative for their safe manufacturing, handling and storage. The evaluation of thermal hazard has usually been through studies of thermal stability using such techniques as differential scanning calorimetry (DSC), differential thermal analysis (DTA), thermogravimetry (TG) and gas evolution (GE). Two characteristic parameters relating to thermal stability, which have been obtained through such studies, are the temperature at which decomposition commences and the activation energy of the decomposition process. Both these parameters may present difficulties in interpretation. Because the thermal decomposition of an explosive is usually a highly exothermic reaction, considerable autocatalysis may occur and the mechanism of the reaction may change as the decomposition proceeds. The rate of decomposition is somewhat ill-defined and difficult to compare from different techniques. For example, rates measured while the temperature is programmed continu-

ously may not be easily related to those measured under isothermal conditions. The derivation of kinetic parameters must therefore be approached with caution. Furthermore, the evaluation of the thermal hazard of an explosive under normal storage conditions from such measurements may involve considerable uncertainty.

In an attempt to address these problems a new technique for the measurement of the thermal stability of reactive materials was developed by Townsend and Tou [1] at the Dow Chemical Company. The accelerating rate calorimeter (ARC) was designed to measure the decomposition of a substance induced by its own heat release. The substance is placed in an adiabatic calorimeter where the heat of the reaction is retained by the material, causing a self-accelerating decomposition. The temperature and pressure in the system are measured continuously as a function of time. Rate measurements are thus obtained under rather different conditions from those found in other techniques. The performance of the ARC and its application to an evaluation of the thermal hazard of energetic materials have been described in the literature [2–5].

The purpose of the present work was the evaluation of kinetic data obtained from an analysis of the self-accelerated rate of decomposition of an explosive material in the ARC. The compound used in this study was tetryl (benzenamine, *N*-methyl-*N*,2,4,6-tetranitro-). Tetryl has been widely used as an explosive in both military and industrial applications, although its health hazard has been recognized and replacements have been examined [6]. The kinetics of its decomposition have been studied since the early twenties [7–17], but the details of the mechanism are not completely understood. Nevertheless its decomposition involves typical features of an explosive reaction and it therefore provides data useful for the present evaluation. In Part I methods for determining the activation energy from the data, following the equations derived by Townsend and Tou [1], are examined for accuracy and consistency. In Part II measurements of the products are related to the stages of the decomposition and compared to similar measurements obtained by other methods.

PRINCIPLES OF OPERATION OF THE ARC

Thermal explosion theory is concerned with the competition between heat generation of the reacting system and heat dissipation from the material to the surroundings. When the rate of heat generation exceeds the rate of heat loss a non-stationary state develops leading to a runaway reaction and explosion. The heat generation is a result of the chemical reaction and its rate will therefore increase exponentially with temperature according to the Arrhenius equation

$$k = Ae^{-E/RT} \quad (1)$$

where k is the rate constant, A is the frequency factor and E is the activation energy for the chemical reaction. The rate of heat loss, on the other hand, is a linear function of temperature. It follows that, for a substance which undergoes an exothermic decomposition there exists a critical temperature beyond which the rate of heat generation exceeds the rate of heat loss and conditions leading to an explosion may develop.

Balancing the increase in rate due to the increase in temperature, is the decrease in rate due to the loss of reactant. If this loss is sufficient the rate of the reaction may pass through a maximum value before an explosion occurs.

In an adiabatic calorimeter the temperature rise after complete reaction is proportional to the amount of material introduced. The amount of material present at any time is therefore proportional to the fractional attainment of the final temperature rise and may be expressed as

$$C = \frac{T_F - T}{T_F - T_0} \times C_0 \text{ or } C = \frac{T_F - T}{\Delta T} \times C_0 \quad (2)$$

where C_0 is the initial concentration, C is the concentration at temperature T and T_F and T_0 are the final and initial temperatures, respectively.

For a reaction of order n , the rate is given by

$$\frac{dC}{dt} = -kC^n \quad (3)$$

The self-heat rate, m_T , is obtained by differentiating eqn. (2) with respect to T and substituting into eqn. (3):

$$m_T = \frac{dT}{dt} = k \left(\frac{T_F - T}{\Delta T} \right)^n \Delta T C_0^{n-1} \quad (4)$$

Equation (4) relates the self-heat, m_T , to the measured temperature, T . Rearranging eqn. (4) defines k^* :

$$k^* = kC_0^{n-1} = \frac{m_T}{\left(\frac{T_F - T}{\Delta T} \right)^n \Delta T} \quad (5)$$

For a first-order reaction, that is, one in which the rate is proportional to the concentration of reacting substance,

$$k^* = k$$

as defined in eqn. (3). The order of a reaction involving the decomposition of a solid material is not well defined because the concentration of a solid material is not a defined property and the characteristic of the solid which is proportional to its rate of decomposition may not be known or may alter as the reaction proceeds. For these reasons a rate constant for decomposition of a solid involves many uncertainties. Nevertheless in many cases the rate of decomposition is approximately proportional to the amount of material undergoing reaction and n may be taken as 1. Equation (5) then becomes

$$k^* = \frac{m_T}{T_F - T} \quad (6)$$

Values of k^* are thus obtained by the measurement of the rate of decomposition as a function of temperature through the complete course of reaction and these data are used to obtain the activation energy for the reaction and to interpret the kinetics of the decomposition.

Thermal inertia

In the accelerating rate calorimeter part of the heat generated from the reaction is used to heat the sample bomb. The property of the system called thermal inertia determines the amount of heat that is lost to the bomb and is defined as follows:

$$\phi = 1 + \frac{M_b C_{vb}}{M_s C_{vs}} \quad (7)$$

where M_b and M_s are the mass of the bomb and the sample, respectively, and C_{vb} and C_{vs} are the heat capacities of the bomb and the sample, respectively. For the latter, an average value of $0.5 \text{ cal } ^\circ\text{C}^{-1}\text{g}^{-1}$ is usually used.

The effect of the thermal inertia is to slow down the reaction by a constant amount. The adiabatic temperature rise of the system is given as

$$\Delta T = \phi \Delta T_s \quad (8)$$

where ΔT is the adiabatic temperature rise and ΔT_s is the temperature rise of the system. In experiments with the ARC the thermal inertia is an important factor in determining the rate of the reaction. For the maximum sensitivity it should be kept low, but a large thermal inertia may be useful in preventing an explosion and for keeping the rate in a measurable range. It may be adjusted by altering the ratio of the weight of material to the weight of the bomb, or by adding an inert solid to the reacting material. Large quantities of material, however, may result in damage to the instrument.

The total heat generated from the decomposition of the material in the bomb, ΔH , is given by the following equation:

$$\Delta H \text{ (cal g}^{-1}\text{)} = C_v \phi \Delta T_s \quad (9)$$

and the molar heat of reaction is therefore

$$\Delta H_m \text{ (cal mol}^{-1}\text{)} = \Delta H \times \text{molecular weight} \quad (10)$$

EXPERIMENTAL

The instrument used in the present experiments was developed at Dow Chemical Company and manufactured by Columbia Scientific Industries of Austin, Texas. A detailed description can be found in the literature and only a brief discussion of the instrument design and operation logic will be given.

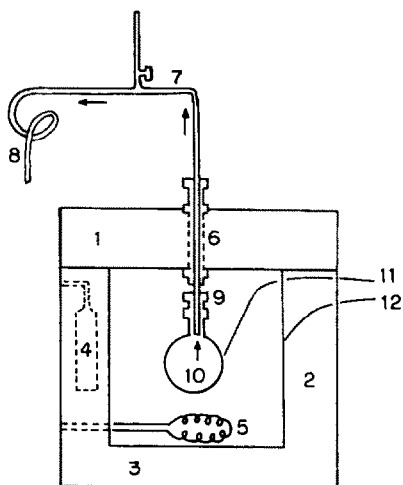


Fig. 1. Schematic diagram of the ARC including bomb and showing the modification to the assembly system: (1) top zone, (2) side zone, (3) bottom zone, (4) cartridge heater, (5) radiant heater, (6) original fixed bomb adaptor, (7) valve, (8) 1/16 in OD stainless-steel tubing connected to pressure transducer, (9) cap connecting the 3/16 in OD filler tube of the bomb to pressure measurement system, (10) sample container (bomb) with 3/16 in OD filler tube, (11) bomb thermocouple, (12) jacket thermocouple.

The calorimeter consists of the bomb and connecting tubing, the jacket containing the heaters and the thermocouples. A diagram is shown in Fig. 1. The bomb and its contents must be maintained adiabatically with respect to the environment throughout the course of a reaction. In the ARC this is achieved over the temperature range of ambient to 500°C with control by a digital thermocouple/heater feedback system. The heating jacket has three zones, individually controlled. The thermocouples are cemented to the inside surface of the jacket and clamped directly on the outside surface of the bomb. The latter are insulated with fibreglass sleeves. All the thermocouples are referenced to the ice point made by Kaye Instruments, which is stable to within 0.01°C. The pressure of the reaction system is monitored with a diaphragm pressure transducer from Sensotec Inc., range 0–2500 psi. The transducer is mounted inside the containment vessel where it is relatively cool. For safety precautions, the entire calorimeter is placed inside a metal compartment.

Difficulties were encountered with the pressure measurement while studying materials which melt before decomposition. The molten material was carried to the connecting line and solidified, causing a blockage. To overcome this problem the original fixed adaptor, connecting the bomb with the pressure gauge, was replaced with a removable connecting line.

All the experiments were conducted in the spherical bomb under an atmosphere of air. In the “confined” system the sample and the bomb were connected to the pressure transducer. The pressure change due to the

decomposition was monitored and the products of the decomposition remained in the bomb. Some decompositions were performed in a “non-confined” system in which the sample bomb was only loosely connected to the pressure measurement line. The pressure in the system did not increase and the products were not confined to the bomb.

Thermocouples

Successful operation of the ARC depends on a sensitive, stable and reliable measurement of temperature. The thermocouples must not be affected by the corrosive conditions in the bomb and must maintain low noise and drift properties. Type N thermocouples meet these requirements. The silicon content of the alloy prevents oxidation. Mismatch may still, however, be a problem. For example, two thermocouples which are perfectly balanced at 25°C may have a difference of up to 15 μV at 300°C. Tou and Whiting [3] reported that the thermocouple attached to the outside of the bomb was reliable for self-heat rates up to 70°C min⁻¹ for the Ti bomb and 20°C min⁻¹ for the Hastelloy C bomb.

Sample bombs

The spherical sample bomb, 1 in OD diameter and 9 ml volume, was used in this study. The bombs were constructed with various materials and wall thicknesses which can tolerate pressures up to 2500 psi. The titanium spherical bomb has low mass (~ 8 g) and low thermal inertia. The Hastelloy C bomb has greater weight (~ 19 g) but was more corrosion-resistant. Both were used in the present study.

Calibration

To achieve adiabatic conditions, the jacket is maintained at the same temperature as the bomb. If drift occurs, an offset value is incorporated into the measured difference to adjust it to the correct value. This calibration is performed incrementally every 50°C over the entire temperature range. The empty bomb can therefore be heated to any temperature while maintaining adiabatic conditions. If a material in the calorimeter undergoes decomposition, a net temperature rise will be due to reaction. The placement and thermal contact of the bomb thermocouples is critical to obtaining reproducible measurements.

Operation

The heat-wait-search operation logic was performed as follows. The ARC was first heated to 100°C and held 30 min for thermal equilibrium before

the rate search operation. If, after the designated wait period the self-heat rate is less than the detection limit, $0.02^{\circ}\text{C min}^{-1}$, the ARC will proceed automatically to the next preselected temperature and again wait to detect a temperature increase. The calorimeter is maintained at adiabatic conditions while the temperature, pressure, self-heat rate and time are recorded, printed and stored in the microprocessor. At the conclusion of the experiment values of k^* , for various values of n , and values of the pressure are plotted as a function of $1/T$ by the microprocessor.

Materials

Tetryl (benzenamine, *N*-methyl-*N*,2,4,6-tetranitro-) was obtained from the Defence Research Establishment at Valcartier, Quebec, in the form of small prills and was stored at room temperature. Silica, 240 mesh, was obtained from Fisher Scientific.

RESULTS

The thermal decomposition of tetryl was studied using both spherical bombs. Experiments were performed with values of the thermal inertia, ϕ , ranging from 7.4 to 21.8 obtained by using different sample weights. The temperature at which decomposition commenced was slightly higher for the experiments with greater thermal inertia. With the Hastelloy C bomb explosion occurred when the value of ϕ was less than 8, causing some damage to the instrument. In one experiment 0.3813 g of tetryl was mixed with 0.4560 g of silica, giving a value of ϕ of 10.3, based on the weight of tetryl. The temperature of the onset of decomposition was the same as observed for the undiluted reactant. Using the Hastelloy C bomb experiments were done in both the "confined" and "non-confined" systems. The temperature at which decomposition commenced was the same in both systems.

The result of a typical decomposition, showing the self-heat rate and the pressure as a function of $1/T$, is given in Fig. 2. It is clear that the decomposition occurred in two stages. From these data values of k^* were obtained as a function of T , by eqn. (5), throughout the course of the decomposition. Equation (5) was tested using values of n of 0.5, 1.0 and 1.5. Values of k^* for these values of n for the two decomposition stages are shown as a function of $1/T$ in Fig. 3. In the usual interpretation of this plot, the value of n which gives a linear relation over the widest temperature range is the most reliable indication of the order of the reaction. A linear relation shows that k^* follows the Arrhenius function and thus may be considered as a true rate constant describing a decomposition path of the explosive. Both stages of the decomposition of tetryl appear to occur by

TABLE 1

Thermal decomposition data of tetryl

Expt.	Weight of tetryl (g)	ϕ	Peak 1		m_0 ($^{\circ}\text{C min}^{-1}$)		T_m ($^{\circ}\text{C}$)	m_m ($^{\circ}\text{C min}^{-1}$)	Activation energy (kcal mol $^{-1}$)														
			T_0 ($^{\circ}\text{C}$)	Peak 1	Method (a)				Method (b)		Method (c)												
					Peak 1	Peak 2			Peak 1	Peak 2	Peak 1	Peak 2											
<i>Hastelloy C bomb</i>																							
155 ^a	0.7300	7.4	136.2	0.03	183.3	161	60	53															
156	0.4256	11.8	141.5	0.04	175.1	2.50	54	46	48														
252	0.2546	18.7	141.0	0.03	159.6	0.26	52	42	40														
291	0.3552	14.2	141.5	0.04	171.5	1.24	51	43	42														
294	0.3550	14.2	141.7	0.05	172.8	1.76	51	43	38														
164 ^b	0.3813	13.0	141.4	0.04	168.5	0.78	52	43	37														
Average values:									52 \pm 1	43 \pm 1	51 \pm 2	41 \pm 3	52 \pm 4										
<i>Titanium bomb</i>																							
274	0.3868	9.1	135.9	0.03	186.5	95.5	51	48															
275	0.2510	13.5	135.9	0.02	170.1	0.88	46	38	36														
276	0.1500	21.8	141.1	0.04	162.2	0.24	48	41	46														
277	0.2520	13.4	136.7	0.04	174.7	1.38	50	39	36														
287	0.3000	11.5	140.8	0.03	176.9	1.95	50	40	42														
288	0.3000	11.4	140.7	0.03	171.9	1.15	50	43	43														
280 ^c	0.3813	10.3	140.9	0.03	181.0	4.00	46	44	44														
Average values:									49 \pm 2	41 \pm 2	46 \pm 2	39 \pm 3	45 \pm 2										

^a Not included in the calculation of average values.^b Non-confined system.^c Mixture of 45% tetryl and 55% silica.

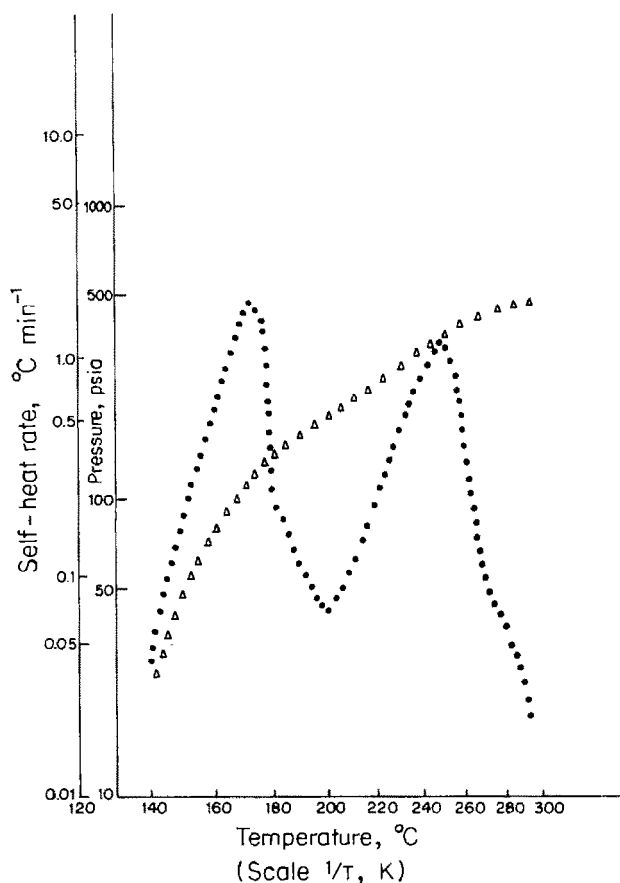


Fig. 2. Self-heat rate (●) and pressure (Δ) as a function of $1/T$. Hastelloy C bomb; $\phi = 14.2$.

first-order processes. The results of the experiments are summarized in Table 1.

Calculation of the activation energy

The activation energy for decomposition is one of the important parameters relating to the stability of an explosive. An activation energy is associated with a particular mechanism or pathway for decomposition and may be determined directly from a measured rate of decomposition. Because of the sensitivity of rate measurements to the conditions of the experiments, as discussed earlier, care must be taken in the calculation of the activation energy from the data and in its interpretation. Three methods for obtaining the activation energy for decomposition of tetryl from the present data will be described, following the equations derived by Townsend and Tou [1]. A comparison of the values obtained by these treatments illustrates the appli-

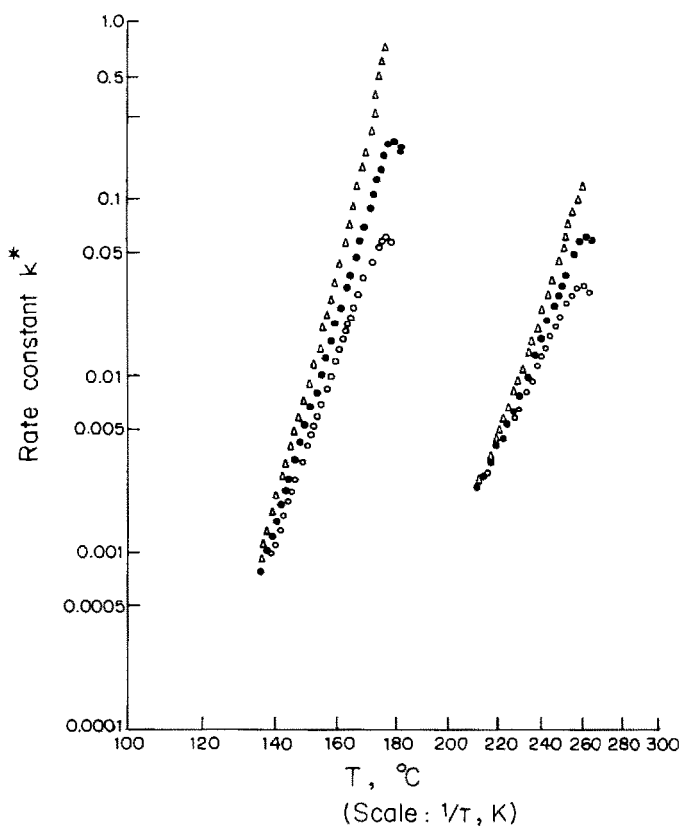


Fig. 3. Rate constant, k^* , as a function of $1/T$. Titanium bomb; $\phi = 13.4$ reaction order, $n = 0.5$ (O), 1.0 (●), 1.5 (Δ).

capability of each method in the interpretation of the mechanism of the decomposition.

*Calculation from k^**

The most direct method for obtaining the activation energy is from the change in k^* with temperature as illustrated in Fig. 3. When $\ln k^*$ is a linear function of $1/T$, the slope is directly related to the activation energy. Values were calculated both from the measured slope or from the printed data points. Results obtained for both decomposition stages are given in Table 1. The activation energy for the first stage of decomposition appeared more reproducible than that obtained for the second stage and was not greatly changed by the use of the non-confined system or of different thermal inertia. Values were, however, slightly lower from the decomposition in the Ti bomb.

A critical factor in the calculation of k^* is the value of T_F , the final temperature after complete decomposition. Because two stages of decom-

position were observed a question arises concerning the separation of the two decomposition peaks and the reliability of T_F measured after the first stage. In the calculation of k^* , T_F was taken at the slowest self-heat rate following the first decomposition. To test the sensitivity of the values of k^* and the activation energy to an error in T_F , k^* was calculated using $T_F \pm 5^\circ\text{C}$. The error introduced into the activation energy ranged from 1 to 4%. For the calculation of the activation energy for the first stage of decomposition therefore the values of T_F appear reliable.

Calculation from the time to maximum rate

The relation between the time to maximum rate and the activation energy of the reaction was discussed by Townsend and Tou [1]. They showed that for reactions with high activation energies, that is, in the range found for tetryl, the time to maximum rate, θ_m , was approximately proportional to $1/k$, the rate constant for decomposition, and hence could be expressed in the Arrhenius form:

$$\ln \theta_m = \frac{E}{R} \left(\frac{1}{T} \right) - \ln A \quad (11)$$

where A is the frequency factor for the reaction.

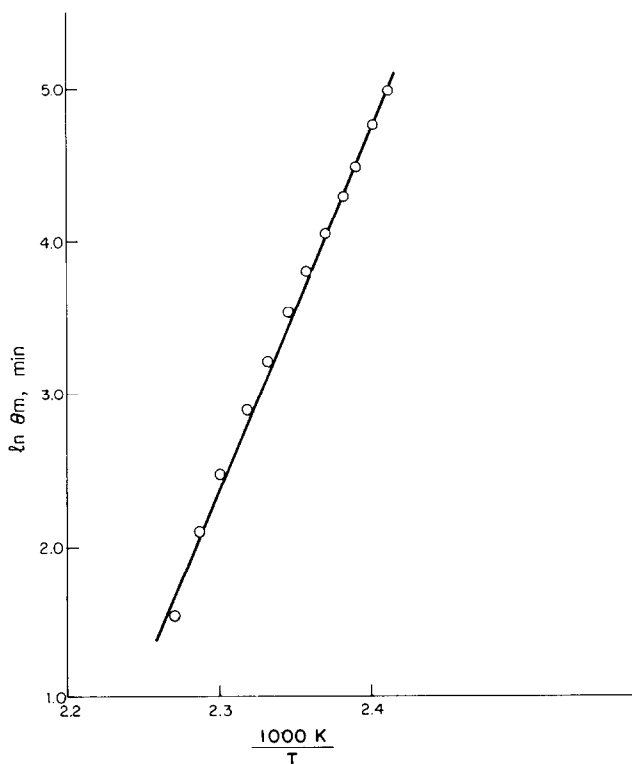


Fig. 4. Time to maximum rate as a function of $1/T$. Hastelloy bomb; $\phi = 14.2$; Peak 1.

The time to maximum rate was calculated for both stages of decomposition and a typical plot is shown in Fig. 4. The values of the activation energies obtained by this method are included in Table 1. The values were in good agreement with those obtained from the first method and again the activation energy obtained from experiments in the Ti bomb was somewhat lower than that obtained from experiments in the Hastelloy C bomb.

Calculation from the initial rate

The previous methods for determination of the activation energy depended on data obtained during the complete, or almost complete, course of the reaction. A limitation of these methods is the occurrence of a very fast rate, preceding ignition or explosion, or a change in mechanism as the decomposition occurs. A third method uses data only in the initial stages of the reaction and therefore provides a useful comparison with the other two.

For a particular reaction, the temperature at which self-decomposition begins to occur is a function of the thermal inertia of the system, since, as discussed earlier, the effect of ϕ is to slow down the reaction by a constant

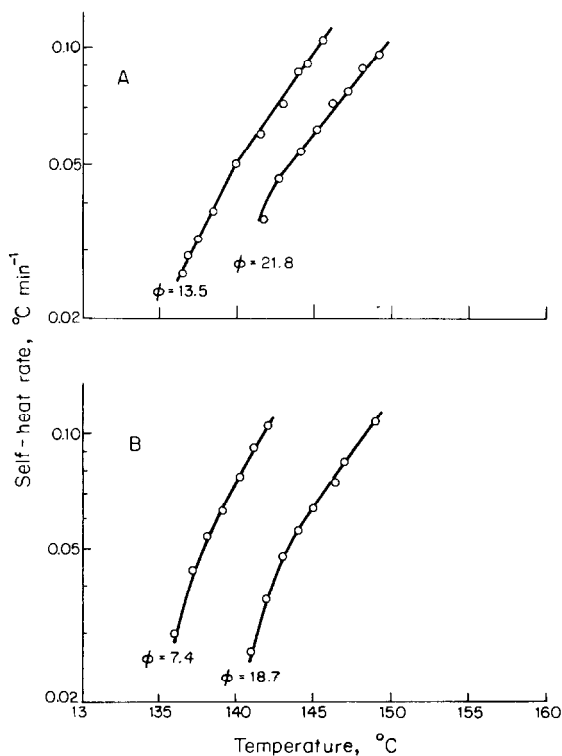


Fig. 5. Self-heat rate as a function of temperature for various values of ϕ . (A) Titanium bomb; (B) Hastalloy C bomb.

amount. This effect will be a function of the activation energy of the decomposition. In general, Townsend and Tou [1] have shown that for a decomposition at low extent of reaction, measured with different thermal inertia, the temperatures corresponding to the same self-heat rate are related to the thermal inertia as follows:

$$\frac{1}{T_2} = \frac{1}{T_1} + \frac{R}{E} \ln \frac{\phi_1}{\phi_2} \quad (12)$$

where T_1 and T_2 are the temperatures where a particular self-heat rate was observed with thermal inertias ϕ_1 and ϕ_2 , respectively.

Since the difference in temperature for different ϕ is not large, the self-heat rates must be accurately and reproducibly measured. To obtain a reliable estimate of T_1 and T_2 , the self-heat rates for different values of ϕ were plotted as a function of temperature. Results from the Ti bomb are shown in Fig. 5A and from the Hastelloy C bomb in Fig. 5B. From the smoothed curves values of T_1 and T_2 were estimated for self-heat rates of 0.05, 0.07, 0.09 and 0.10 °C min⁻¹ and the average values are given in Table 2.

Activation energies for the decomposition of tetryl from this method gave a range of values which for both bombs appeared to decrease as the value of the self-heat rate increased. The method is certainly less accurate than the other two because of the difficulty in estimating small values of the temperature difference. The average values are, however, close to those from the other methods for the same bomb.

TABLE 2

Calculation of the activation energy from the relation between the self-heat rate, the temperature and the thermal inertia

Self-heat rate (°C min ⁻¹)	Temperature (°C)	Activation energy (kcal mol ⁻¹)
<i>Hastelloy C bomb</i>		
	$\phi = 7.4$	$\phi = 18.7$
0.05	137.7	143.3
0.07	139.7	145.5
0.09	141.0	147.5
0.10	141.7	148.5
<i>Titanium bomb</i>		
	$\phi = 13.5$	$\phi = 21.8$
0.05	140.0	143.5
0.07	142.7	146.3
0.09	144.5	148.4
0.10	145.3	149.3

DISCUSSION

A summary of the measured activation energies is given in Table 1. The values from the three methods are in good agreement for a particular bomb, but there is a significant difference in the values obtained for each bomb. This is also apparent in the differences in the initial temperature of decomposition observed for each bomb for comparable values of ϕ . This difference may reflect the different thermal conductivity of the bombs which determines the speed of the response of the system to the heat released by the reaction. In an autocatalytic reaction even small heat losses will have a large effect on the rate of decomposition which in turn determines the rate of change of temperature with time and the value of the activation energy. The significance of the value of the activation energy is discussed in relation to the values obtained by other techniques in the following paragraphs.

The present results are compared with other measurements of the decomposition of tetryl, summarized in Table 3. Inspection of this table reveals that the Arrhenius parameters obtained from rates measured isothermally are in reasonable agreement, with an average value of 36 kcal mol^{-1} for the activation energy and 10^{13} s^{-1} for the frequency factor. The latter may be considered reasonable for a dissociation involving the breaking of bonds. On the other hand, measurements of the rate made with increasing temperature, which includes measurements by DTA, DSC and the present results by ARC, given, with one exception, significantly higher values for the activation energy, in the range $52\text{--}76 \text{ kcal mol}^{-1}$. These high activation energies, which were obtained within the temperature range spanned by the isother-

TABLE 3
Measured activation energies for the decomposition of tetryl

Technique	Temperature range (°C)	Activation energy (kcal mol ⁻¹)	Frequency factor, log A (s ⁻¹)	Reference
Isothermal	120–140	36.6	12.7	Farmer [7]
Isothermal	211–260	38.4	15.4	Robertson [9]
Isothermal	132–164	35	12.9	Cook and Abegg [10]
Isothermal	140–160	35.2	13.5	Dubovitskii et al. [11]
DTA	162	76		Krien [13]
DSC		55		Rogers and Morris [14]
DSC	170–174	58		Hall [15]
Isothermal	140–170	41		Hara and Osada [16]
DTA	170	41		Hara and Osada [16]
Isothermal	180–205	32	13.2	Hutchinson [6]
ARC	140–180	52	23	present work

mal measurements, do not indicate an exceptionally slow rate for decomposition. From the present measurements a pseudo-first-order rate constant was derived which, at a temperature of $\sim 140^\circ\text{C}$ was within the range of values obtained isothermally. With increasing temperature, however, the rate constant increased very rapidly, giving an apparently high value for the activation energy and leading to a value of 10^{23} s^{-1} for the frequency factor. This result, which is impossibly high for any simple dissociation reaction points to the reason, if not the explanation, for the discrepancy between the results of the isothermal studies and those made with increasing temperature.

Empirically, when tetryl is subjected to increasing temperature, the rate of decomposition increases much faster than predicted by a consideration of the Arrhenius energy barrier measured isothermally. This may be an effect of the autocatalytic processes on the rate, but the result is both a higher temperature coefficient for the rate constant and a higher frequency factor than measured isothermally. In such a situation it is surprising that the pseudo first-order rate constant appears to follow an Arrhenius behaviour over a wide range of temperature. Nevertheless the empirical activation energy obtained from these experiments cannot be simply interpreted in terms of a particular energy barrier for the decomposition process. On the contrary, such results (high activation energy coupled with a high frequency factor) can probably be taken to indicate a high sensitivity to autocatalysis and a tendency to undergo a runaway decomposition. In this sense the results obtained from techniques using increasing temperatures may be valuable in the assessment of thermal hazards. It should be noted, however, that for this interpretation values for both the activation energy and the frequency factor are required and that rate constants for the decomposition are more readily derived from results obtained from the ARC than from DSC or DTA.

An early study of the isothermal decomposition of tetryl [7] had reported results which led to very similar "high" values for the activation energy and the frequency factor. These results were subsequently shown [15] to be caused by a large difference in the rate of decomposition between solid and liquid tetryl. A combination of the rates measured in solid and liquid phases gave an apparent activation energy of 60 kcal mol^{-1} and a frequency factor of 10^{27} s^{-1} . Other observations [8] of increased rate of decomposition of the solid were explained in terms of a lowering of the melting point of tetryl caused by additives or small amounts of products [18]. Although it was concluded that no particular significance could be attached to these values of the activation energy and frequency factor, the reason for the increased rate of decomposition of the liquid has not been adequately explained in terms of molecular dissociation processes. It is unlikely that the reasons are related to the causes of the anomalous behaviour of the decomposition in the ARC, although the empirical results are similar.

CONCLUSION

The kinetics of the thermal decomposition of tetryl have been analysed using results obtained with an ARC. Three methods have been used to obtain an activation energy for the decomposition and their limitations discussed. The range of values for the activation energy reported in the literature has been rationalized from the point of view of the technique used in the measurements.

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