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A STUDY OF THE THERMAL DECOMPOSITION OF CONFINED TRIAMINOTRINITROBENZENE. THE GASEOUS PRODUCTS AND KINETICS OF EVOLUTION *

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ABSTRACT

The thermal decomposition of confined triaminotrinitrobenzene (TATB) has been studied by observation of infrared matrix isolation spectra, mass spectra, and pressure–time response of the product gases. Solid state products were examined by infrared spectroscopy and scanning electron microscopy. Four distinct reaction regimes were found using the gaseous product data; a slow endothermic stage followed by two slow exothermic stages, and culminating in a deflagration (explosive) reaction above the critical temperature.

INTRODUCTION

The unusual stability of triaminotrinitrobenzene (TATB) arises because of the presence of a large number of intra- and intermolecular hydrogen bonds [1]. This stability is reflected in its thermal decomposition kinetics. The decomposition of unconfined TATB has been the subject of several investigations [2–6]. Integral thermal decomposition kinetics of confined TATB, using the one-dimensional time-to-explosion (ODTX) technique, have been reported [7] as have Henkin tests [8].

This report is of a preliminary investigation of thermal decomposition kinetics for confined TATB. Infrared matrix isolation spectroscopy, mass spectroscopy and pressure–time measurement techniques were applied in order to identify the gaseous products and to measure their rates of evolution. Solid state products were examined by infrared spectroscopy, optical microscopy, and scanning electron microscopy in attempts to identify the solid phases present after an isothermal run. The results of the latter investigation are the subject of a separate report [9]. Both chemical product identification and their isothermal rates of production are necessary to

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determine any reaction mechanism. While not enough information was generated in these experiments to attempt more than primitive mechanistic interpretations, efforts were made to distinguish between time regimes in which apparent individual reactions, or sets of reactions, lead to decomposition.

EXPERIMENTAL

High purity TATB (internal LLNL label B-602, analysis in ref. [5], Table 1) was pressed into a sample assembly. The left side of Fig. 1 is a schematic of the sample vessel which consisted of a modified air-operated Nupro valve. This assembly was mounted onto a hydraulic cylinder for convenient immersion into and out of a heat bath.

Controlled air pressure was applied to the actuator of the Nupro valve assembly to maintain a confinement pressure of 10,000 p.s.i. on the TATB sample during the course of each experiment.

Several heating arrangements were used during the course of the experiments in continuous attempts to minimize temperature gradients within the samples. These were (1) a Cu block with cartridge heaters and heater coils, (2) a heating jacket, (3) a sand bath, (4) an oil bath, and (5) a fluorocarbon oil bath (non-flammable). The oil baths were the most successful, but thermal gradients could not be entirely eliminated because of the complex shape and large mass (~ 200 g) of the sample valve assembly. The thermal gradients are the largest sources of error in this study. Sources of non-reproducibility were temperature variation, typically ±0.75°C, and the time required for the sample to reach temperature.

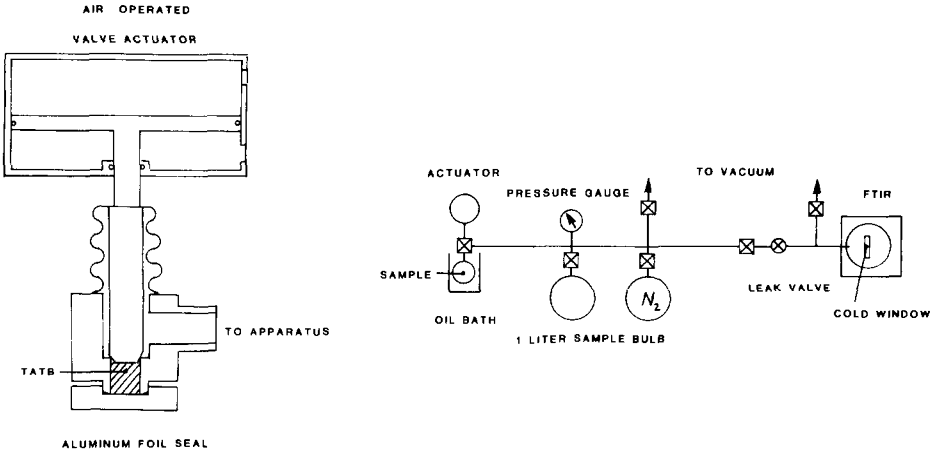

Fig. 1. Schematic of apparatus. Left side schematically shows the sample valve assembly. Right side illustrates matrix isolation apparatus.

At the start of a run, the sample assembly was plunged into the regulated temperature bath. The temperature at one surface of the sample was continuously monitored. The right side of Fig. 1 is a schematic of the sample collection and preparation system. It also schematically illustrates the matrix isolation apparatus. When decomposition occurred, the pressure above the sample would increase due to the evolution of gaseous decomposition products. When the pressure exceeded 10,000 p.s.i. the valve opened and the products were collected in a 1 l glass flask. The valve closed again as soon as the pressure decreased below 10,000 p.s.i. At the end of the run the sample was quickly removed from the bath and cooled almost to room temperature to avoid condensation of high vapor pressure solid products in the vacuum lines. The valve was then manually opened to collect any remaining gaseous products.

The pressure of the collected gaseous decomposition products was measured and a large excess of N_2 was introduced into the collection flask. The gases were mixed and then sprayed onto a CsI window at ~ 11 K. Standard matrix isolation techniques were used [10] in the conventional continuous deposition mode. The objective was to isolate molecules of the gaseous decomposition products and hold them rigidly in a "cage" of the N_2 crystal lattice, thus eliminating the rotational bands in the IR spectra. A large ratio of N_2 : gas ensured a separation between the sample gas molecules and eliminated formation of dimers, all of which greatly simplified the recorded IR spectra and their interpretation.

The matrix isolation spectra were obtained with a Fourier Transform Infrared (FTIR) spectrometer. These spectra showed only the Q branches of bands due to the vibrational modes of the gaseous product molecules, and appeared as if they were line spectra.

Samples for mass spectroscopic analyses were also collected in the 1 l flasks at the conclusion of pressure vs. time runs. The pressure measured was that of the collected product gases.

RESULTS AND DISCUSSION

Seventeen isothermal runs were made on approximately 0.5 g samples of TATB at temperatures and times ranging from 202°C for 38.5 h to 312°C for 3 min. Matrix isolation spectra were obtained on thirteen runs, and mass spectroscopy samples were taken for five pressure vs. time runs.

Product gases were identified by using both matrix isolation spectroscopy and mass spectroscopy. Comparison of various IR spectra of matrix isolated samples of gaseous product from isothermal runs showed that there were two distinctly different sets of products. In the short time runs, the spectral bands due to CO_2 and H_2O were the only ones found; in the longer runs, other product bands occurred in addition to those of CO_2 and H_2O (Fig. 2).

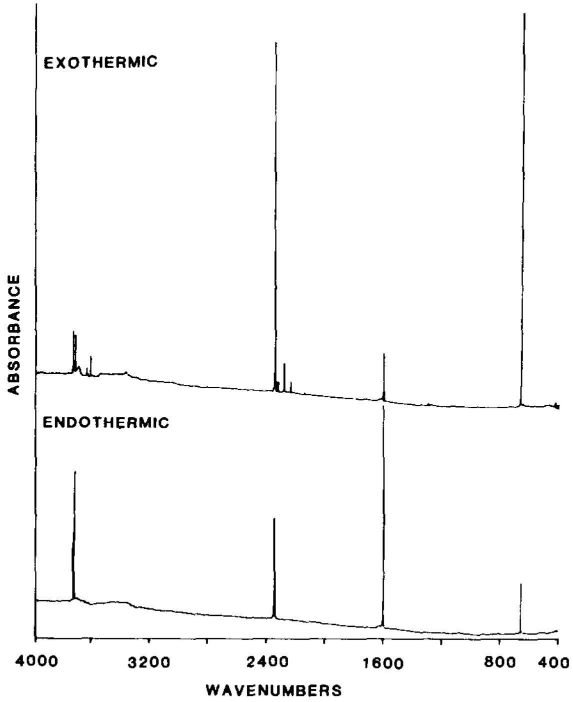

Fig. 2. Typical matrix isolation spectra of gaseous products.

Ammonia should have been a product according to reports of the decomposition of unconfined TATB [3]. However, as long as NH_3, CO_2, and H_2O were present such that $[NH_3] < [CO_2]$ and $[H_2O]$, detection of NH_3 was not possible, since NH_4HCO_3 would precipitate on the walls of the vacuum system. Ammonia was never seen in either our matrix spectra or mass spectra. Another difficulty was that the ratios $[CO_2]:[H_2O]$, derived from matrix runs at approximately the same temperature, showed no correlations with pressures of collected gas or time. Despite these difficulties and despite problems with thermal gradients across the sample container during decomposition, much useful information was obtained.

At the termination of the heating period, the sample was quickly removed from the heat bath while the pressure of the collected product gas was monitored. If the pressure continued to rise, we assumed the decomposition to be exothermic. If it did not, the decomposition was assumed to be endothermic. Such responses could not differentiate small thermal effects and are only qualitative. The spectra containing only CO_2 and H_2O came from experiments, presumably endothermic, for which the pressure did not rise after the removal of the heat bath. The more complex spectra came from samples for which the pressure continued to rise after the source of heat was removed and, therefore, correspond to exothermic reactions. The complexity of the mass spectra parallels the matrix spectra results.

The "raw" kinetics of the decomposition were monitored by using the pressure of evolved product gases. If the reaction was

$$\mathrm{TATB}_{\mathrm{solid}} \rightarrow \mathrm{B}_{\mathrm{solid}} + \mathrm{C}_{\mathrm{gas}} \tag{1}$$

then the pressure, $P(t)$, obtained as a function of time in isothermal experiments would represent the extent of reaction and would be proportional to the fraction of TATB reacted, α, during time t

$$P(t) = k\alpha(t) \tag{2}$$

where P is a relatively simple function

$$P = P(\alpha) \tag{3}$$

On the other hand, the decomposition of any but the very simplest of explosives is expected to consist of sets of consecutive and/or concurrent reactions. If the TATB decomposition is indeed complex, as expected, then

$$P(t) = \mathrm{f}(\alpha, t) \neq k\alpha(t) \tag{4}$$

where P depends upon both α and t. For this discussion, we treat the data as if eqn. (2) holds either over the entire decomposition or piecewise, and then attempt to interpret some portions of the decomposition isotherms. Reaction mechanism interpretations based on such a treatment can at best only be indicators pointing toward further research. However, there is no reason that the data analyzed in such a treatment could not be used in a semi-empirical manner for predictive purposes.

Pressure vs. time

Figure 3 is a plot of pressure vs. time for several isothermal runs. We define an empirical time-to-explosion (t_x), determined by the heat-flow characteristics of the sample assembly and of the integral decomposition reaction kinetics of TATB, to be given by the vertical asymptote of $P(t)$. The measured t_x values were almost equal to the t_x values from ODTX experiments [7] at lowest temperatures and longer by about a factor of two at highest temperatures. This agreement is quite satisfactory and reflects the basic similarities between the two techniques. The complex behavior of the data taken at a nominal 240°C for long times is undoubtedly due to thermal instability of the oil bath combined with a temperature which is low enough to be close to the critical temperature. The critical temperature is that temperature above which heat-flow out of the sample is too small to prevent self heating from the exothermic decomposition, leading to deflagration or thermal explosion. When the system is very near the critical temperature, instabilities are to be expected.

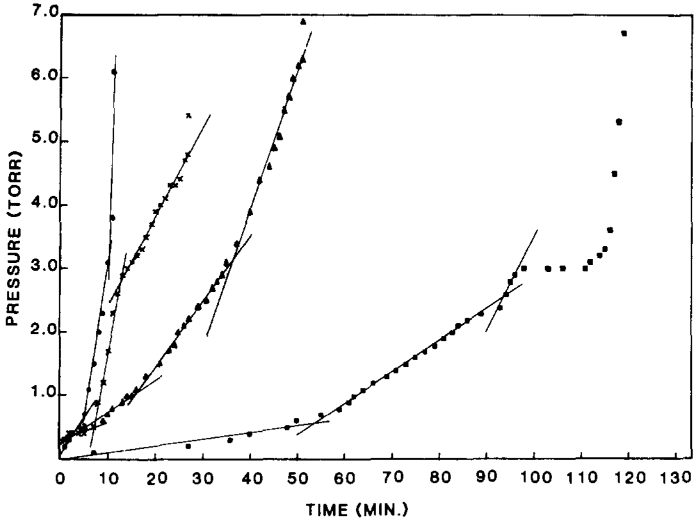

Fig. 3. Pressure of gaseous products vs. time. ●, 301°C; ×, 282°C; ▲, 261°C; ■, 240°C.

Extent of reaction

The total pressure rise when a sample has gone to explosion, P_x, represents 100% of the extent of reaction for any given sample temperature. We assume that P_x does not change with decomposition temperature; that is, the number of moles of product gas per mole of TATB is constant as long as the decomposition is carried out above the critical temperature. (However, we have no data to substantiate this assumption.) Using the data in Fig. 3 and an experimental value for P_x of 134 Torr of product gases after explosion

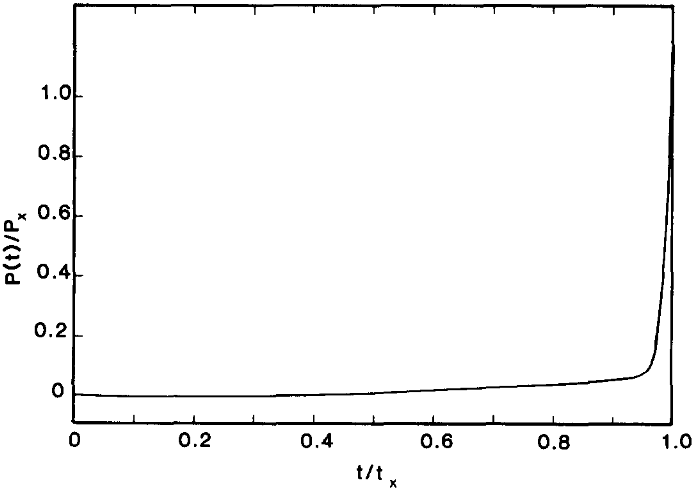

Fig. 4. Percent reaction vs. percent of time-to-explosion for confined TATB.

when $t \simeq 0.95\ t_x$, (taken from a matrix spectroscopy run that went to explosion), the extent of reaction is of the order of 5%.

The curve in Fig. 4 is representative of the reduced pressure, $P(t)/P_x$, behavior with reduced time, t/t_x, at any temperature. It schematically represents the extent of reaction as t approaches t_x and gives integral raw kinetics complementary in form to ODTX data [7]. Plotted on the scale as shown, details in $P(t)$ are smeared out. Without the higher resolution pressure data, the slow buildup of reaction (slow in terms of t/t_x) would imply an induction time. This coarse viewpoint of the data, implies that eqn. (2) is a reasonable assumption up to $t/t_x \simeq 0.95$. (But, the treatment of the data may be deceptive in that eqn. (2) was assumed valid for these experiments. Also, the concept of an induction time for reactions that are consecutive and/or concurrent may be ambiguous.)

Corresponding reactions

In general, while explosive decomposition suggests extreme complexity, it is possible that for TATB the reactions might be consecutive, with each region corresponding to another in the same sequence for different isotherms. If this is the case, a set of corresponding reactions can be found. The procedure for finding such corresponding reactions is analogous to that for defining corresponding states in chemical thermodynamics. We now examine the $P(t)$ data in detail in which the correspondence is sought by the analysis of the data in terms of reduced variables [11]. The data from Fig. 3 is plotted in a reduced dimensionless form with $P(t)/P_8$ vs. t/t_x as the coordinates in Fig. 5. In order to expand the ordinate in Fig. 5, a point in all isothermal

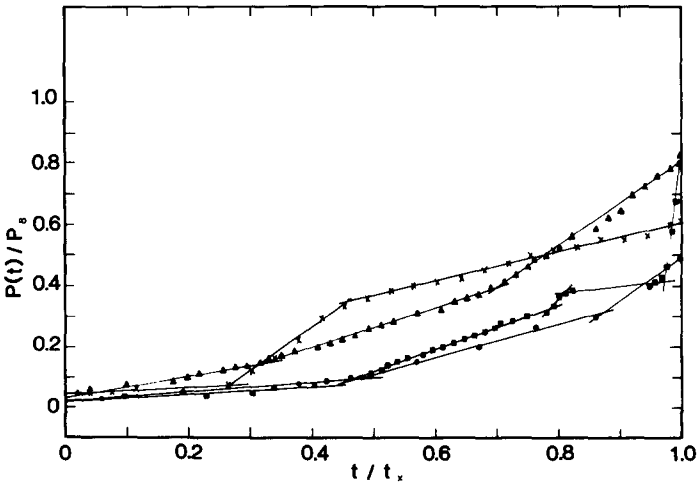

Fig. 5. Corresponding reactions plot for confined TATB. ●, 301°C; ×, 282°C; ▲, 261°C; ■, 240°C.

TABLE 1

A. Mass spectroscopy

	Amount of Products (millimoles)								
	240°C		262°C		282°C		301°C		312°C Explosion
Products	Endo	Exo	Endo	Exo	Endo	Exo	Endo	Exo	
CO_2	0.0314	0.497	0.0169	0.209	0.0209	0.181	0.00482	0.207	1.15
H_2O	0.007	0.001	0.015	0.044	0.017	0.042	0.007	0.033	0.03
N_2	0.0170	0.195	0.0147	0.106	0.0156	0.103	0.005	0.121	1.83
H_2	0.000834	0.000712	0.000385	0.000769	0.00417	0.00139	0.00164	0.00313	0.325
$(CH_3)_2CO$	0.00026	–	0.0019	0.0027	0.0032	0.0024	0.0068	0.0051	–
NO	0.0016	0.0029	0.0026	0.0058	0.0010	0.0028	0.00015	0.0070	0.719
O_2	0.000641	0.000712	0.00212	0.00115	0.000898	0.00139	0.0256	–	–
HCN	0.000641	–	0.00090	0.0027	0.00039	–	–	0.0031	1.61
CH_4	0.00398	0.00854	0.000385	0.000769	0.000385	0.00045	–	–	–
ϕNO_2	0.00019	–	0.00051	0.00019	0.00026	0.00014	0.00018	0.000051	–
C_2N_2	0.000090	–	0.00013	0.00038	0.000058	0.00014	–	0.00055	0.359
CO	–	0.0064	–	0.011	–	0.0087	–	0.011	2.51
CH_3NO_2	–	0.0071	–	–	–	–	–	0.000026	–
Ar	–	–	–	–	–	–	–	–	0.00684
Alkanes	–	–	–	–	–	–	–	–	0.051

B. Matrix isolation – IR spectroscopy

Products	Endothermic						Exothermic		Explo-sion
	202°C	256°C	260°C	262°C	267°C	306°C	232°C	264°C	312°C
CO_2	X	X	X	X	X	X	X	X	X
H_2O	X	X	X	X	X	X	X	X	X
CO							X	X	X
NO									X
NO_2							X	X	X
N_2O							X	X	X
$(H_2O)_2$							X	X	X
Unidentified bands (≈ 2332 cm^{-1})							X	X	X

TABLE 2

Gas phase product correlation

Region	Endothermic	Exothermic	Explosion
Major components	CO_2 H_2O N_2 $(CH_3)_2CO$	CO_2 N_2 H_2O	CO_2 CO HCN N_2
Medium components			NO
Minor components	CO N_2O NO NO_2 H_2 CH_4	CO N_2O NO NO_2 H_2 CH_4	C_2N_2 H_2 CH_4 H_2O

runs which was well into the vertical asymptote region (explosion region) of Fig. 3, $P = 8$ Torr (P_8), was used instead of P_x.

Examination of Fig. 5 indicates that there is at least an approximate correspondence in that each isothermal reaction consists of four separate stages. Three of these stages are defined by straight lines through the data. The first stage of each reaction isotherm corresponds to what we took to be an endothermic reaction; the intermediate stages correspond to two separate, slow exothermic reactions; the fourth stage near t_x corresponds to explosion. It thus appears as if the confined TATB decomposition can be described phenomenologically as a series of consecutive reactions culminating in an explosive reaction. The latter entails chain and/or concurrent reactions.

This procedure indicates that some correspondence of reactions remains as temperature is varied. If (1) each consecutive reaction could be exactly separated, (2) each had the same mechanism and obeyed the same rate equation as a function of temperature, and (3) there are no chain and/or concurrent reactions, then, all of the plots in Fig. 5 would exactly superpose and the reactions would be isokinetic. (A semi-empirical numerical procedure, designed to aid in identifying rate laws for single solid state chemical reactions has been developed by Sharp et al. [12] based on a technique of Geiss [13]. This technique can also be used to determine isokinetic behavior. However, the stringent requirements on precision and accuracy of the experimental data are virtually impossible to obtain.)

Reaction rates

Since each segment of data in Figs. 3 and 5 is linear in $P(t)$ vs. t, the reaction order for each stage is zero. The rate constants, k, for each of the first three decomposition stages, are related to temperature by an Arrhenius equation

$$k = A\ e^{-E_A/RT} \quad (5)$$

where A is a constant, E_A is an activation energy, T is temperature, and R is the gas constant. The activation energies obtained from plots of $\ln k$ vs. $1/T$ are ~ 20 kcal $mole^{-1}$ for all three stages (endothermic followed by the two exothermic stages). An Arrhenius equation description for the explosive stage of the decomposition is probably inappropriate.

Gas phase products

Matrix spectra and mass spectra were taken of product gases generated from various samples during endothermic and exothermic stages of decomposition isotherms and also from a sample that went to explosion. Table 1 shows the raw data and we have characterized trends in Table 2.

Ammonia might have been a product but was not detected because of the presence of CO_2 and H_2O which would cause solid NH_4HCO_3 to form. Note that the amounts of gaseous products were extremely small for the endothermic samples and quite small for the exothermic samples, since the rate of thermal decomposition was low until $t \simeq 0.95\ t_x$. Acetone was observed in the endothermic samples and was probably an impurity introduced in a TATB purification process. No molecules indicating impurities from other probable solvents, such as those containing chlorine or sulfur, were detected in any of the gaseous products. Ammonium chloride, a common impurity, would not have been detected. The amount of acetone found in the endothermic samples was consistent with an impurity, corresponding to approximately 10^{-4} cm^3 of liquid in the sample. We assume that the alkanes that were detected, particularly in the endothermic samples, arose from the thermal decomposition of acetone [14] and not from the decomposition of TATB.

Several conclusions can be reached.

(a) The gases CO_2, H_2, and H_2O were products at all temperatures.

(b) The quantity of air in the samples examined by mass spectroscopy was too small to account for the N_2 found. Air was determined using Ar and O_2 as markers.

(c) A comparison of N_2, CO_2, and H_2O produced from endothermic and exothermic reactions as a function of temperature (Table 2) indicates that the percentages found were almost constant at all temperatures.

(d) No correlations could be made from the ratios of $[CO_2]/[H_2O]$ in the matrix spectra.

(e) The only products observed from endothermic samples by matrix spectroscopy were CO_2 and H_2O.

(f) The gases NO, N_2O and NO_2 were detected only in exothermic samples.

(g) Mass spectroscopic determinations resulted in identification of components which could not be observed by matrix spectroscopy and with higher sensitivity than the matrix spectroscopy for some components.

Based on the mass spectral data of gaseous products from a sample that exploded (312°C), the overall equation for thermal decomposition is

$$\begin{aligned} C_6N_6H_6O_6 \rightarrow\ & 0.94\ N_2 + 0.01\ H_2O + 0.59\ CO_2 + 1.29\ CO \\ & + 0.17\ H_2 + 0.18\ C_2N_2 + 0.83\ HCN + 0.37\ NO \\ & + \text{solid containing C,N,H, and O} \end{aligned} \tag{5}$$

Note that the data we have obtained indicates that H_2O is not a major product. This conclusion is not firm because NH_3 may have been a product which would have caused an apparent deficiency of CO_2 and H_2O.

CONCLUSIONS

The thermal decomposition of TATB is expected to arise from a series of consecutive and/or concurrent reactions starting with an endothermic step and ending in thermal explosion. The latter is probably a chain reaction or a combination of chain and concurrent reactions. Figures 3 and 5 combined with the direct observation of exo- or endothermicity and changes of pressure of products show four reaction stages. [Recall, however, that the data was treated with the assumption that eqn. (2) is valid.] All of the endo- and exothermic reaction steps had zero order with activation energies of ~ 20 kcal $mole^{-1}$.

We can describe the integral decomposition kinetics for these experiments

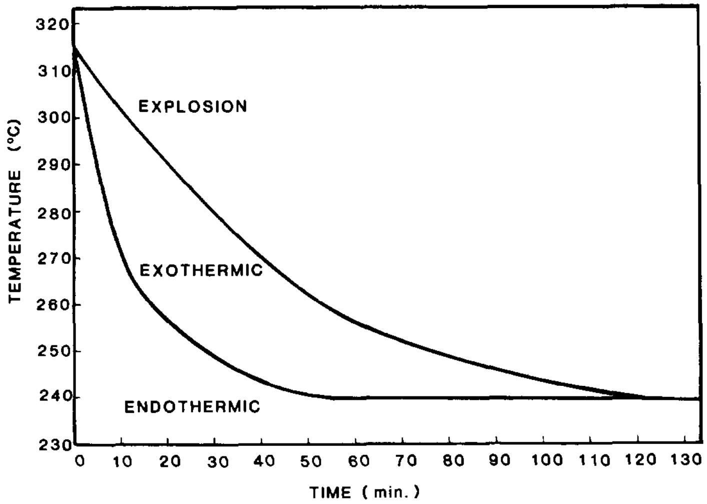

Fig. 6. Integral kinetics plot.

by combining the ODTX data [7] with our present observations. Figure 6 illustrates this approach. It represents a more detailed description than ODTX results alone were capable of giving.

We assume that the endothermic stage of the reaction is removal of H_2O, N_2, CO_2, and acetone that was intercalated in the TATB crystal lattice. The total amounts of H_2O, H_2, CO_2, and acetone removed in this stage indicates that 1 or 2% of the spaces between the planes had been occupied by these molecules. While the removal of intercalated H_2O, N_2 and CO_2 is a plausible interpretation for the decomposition mechanism during this endothermic stage, there are some difficulties which require resolution. The ratios $[CO_2]/[H_2]$ and $[CO_2]/[N_2]$ are too large in a number of samples for air to be the source of CO_2. However, it is probable that the TATB lattice preferentially absorbs CO_2. We can offer no explanation for the origin of H_2; its polarizability is so small that dispersion force stabilization as an intercalate should not be significant to TATB.

Intercalated small molecules can be removed by diffusion, either with or without lattice expansion. The expansivity perpendicular to the crystalline planes is very large [15]. Andrews et al. [3] and Garza [6] found evidence from some of their unconfined heating experiments at low temperatures that water is lost by diffusion. The mechanism suggested by Andrews et al. [3] for initial decomposition of unconfined TATB decomposition at low temperatures involves abstraction of H_2O from intramolecular hydrogen bonds between amino and nitro groups followed by diffusion out of the lattice. A direct comparison of our confined TATB decompositions and the experiments reported by Andrews et al. [3] is not possible since all of our experiments were carried out at considerably higher temperatures (200–300°C). However, interpretation in which CO_2 and N_2 are split off the TATB by ring breaking in the initial, endothermic stage does not seem plausible. While there are small changes in the gaseous product compositions in going from the endo- to exothermic stages, the more significant changes are in the amounts of the gaseous products released. The amounts of CO_2, H_2O, N_2 and H_2 released in these stages are too large to be accounted for by the release of intercalates.

We believe that intramolecular water abstraction cannot be an important mechanism since so little water is released.

SUMMARY

Our data has shown that there are three slow reaction stages in the isothermal, confined decomposition of TATB; an endothermic stage followed by two exothermic stages. Ultimately, the decomposition goes into thermal runaway. We believe that our data shows that the initial, endothermic stage of the decomposition involves the removal of intercalated molecular species by diffusion. None of our data on confined TATB is consistent with an internal H_2O abstraction reaction taking place.

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