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AN ENTHALPIC STUDY OF THE THERMAL DECOMPOSITION OF UNCONFINED TRIAMINOTRINITROBENZENE

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ABSTRACT

The thermal decomposition of triaminotrinitrobenzene (TATB) under unconfined conditions has been studied by isothermal calorimetric techniques using a differential scanning calorimeter (DSC) between 578 and 630 K. The decomposition is exothermic over the entire range. Between $615 < T < 630$ K, the isothermal decomposition data indicates perhaps as many as five distinct reaction stages. Activation energies for each of the five steps are calculated by fitting the data to established solid state kinetic rate-laws.

INTRODUCTION

The unusual stability of triaminotrinitrobenzene (TATB) arises because of the presence of a large number of intra- and intermolecular hydrogen bonds [1].

Previous work suggested that the initial steps in the thermal decomposition of unconfined TATB at temperatures below 455 K involve the abstraction of water followed by diffusion of the water out of the planar crystalline lattice [2]. With increasing temperature, ammonia has been observed as a product [2]. Farber and Srivastava [3] found large molecular weight radical fragments at 523 K in a Knudsen cell–mass spectroscopic investigation. Sublimation of TATB has been reported at low temperatures (< 573 K) [4–6]. Garza [4] found H_2O as the only species besides TATB vapor. Above 600 K, a condensate has also been observed which has a crystal structure very similar to, but not identical with TATB [7,8]. The interplanar spacing lines were very clearly seen and the distances between planes are the same as for TATB. But lines from within the sheets were fuzzy, indicating disorder within the sheets. This may be due to a strained form of TATB. We call attention to this distinction, since the reaction kinetics of polymorphs can be different, even though the chemical formulas are the same.

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In this study, we report on a preliminary investigation of the global thermal decomposition kinetics of TATB under unconfined conditions by isothermal calorimetric techniques. Examination of the solid state products in this study is the subject of a separate report [9].

EXPERIMENTAL

High purity TATB (internal LLNL label B-602, analysis in Table 1) was used. A Perkin Elmer DSC-2 differential scanning calorimeter (DSC) using a nitrogen flow of 10 cm^3 min^{-1} was used to determine the enthalpic changes for the samples held isothermally at various temperatures. Volatile DSC sample pans with a pinhole in the lids were weighed, filled with TATB, crimped closed and reweighed. Sample sizes ranged from 3.00 to 3.16 mg. The calorimeter cell was raised to the desired running temperature and held there for a minimum of two minutes. The samples were dropped into the hot calorimeter cup which was immediately covered. After an equilibration time of approximately one minute (when the recorder pen was on scale), data acquisition began. Both analog and digital data were recorded. Upon completion of the run, residue weights were also recorded. Runs were made between 578 and 630 K (Table 2).

In addition to calorimetric runs, we also made runs to collect the yellow condensate and the black residue for characterization. The condensate was collected by laying a microscope cover slide over the calorimeter cell during the run. The slide and the guard ring insert on which some condensate deposited, were weighed before and after the run. The gain in the weight of these two gave the weight of condensate. A small correction was made to

TABLE 1

Analysis of TATB (LLNL B-602)

Element	ppm	Element	ppm	Element	ppm
K	9	Ni	9	Ag	0.3
P	< 20	Pb	< 3	Cr	3
Si	60	Al	7	Mn	0.3
Fe	30	B	0.9	Na	0.3
Ca	60	Mg	6	Sr	0.6
Cu	0.9	Ti	3	Li	0.2

Elements not detected: Nb, Sb, Zr, Rb, V, Zn (< 9 ppm)
Ba, Bi, Cd, Sn, Be, Cu, Mo (< 0.9 ppm)
DMSO soluble: 0.06 wt.%
Total chloride: 0.04 wt.%
Inorganic chloride: 0.01 wt.%

account for the gap in the guard ring insert. The use of the cover slide hampered the escape of the nitrogen, used as flow gas, and of gaseous reaction products.

The differential power signal (primary data) was read with a digital voltmeter and recorded under computer control at one second intervals from the time the recorder pen was on scale until the end of the run. Data was stored on a magnetic disk. The data was converted to mcal mmole^{-1} and also baseline corrected. Data acquired below 615 K was not processed because these runs (Table 2) were irreproducible and also very lengthy.

RESULTS

Figure 1 is a baseline corrected plot of the change of enthalpy (H) of the sample (dH/dt in mcal sec^{-1} mmole^{-1}) vs. time (t) in seconds for temperatures between 615 and 630 K. The measurement is of enthalpy, since the heat of the reaction, Q, is released at constant pressure (ambient). The data are all plotted on one graph to illustrate the time scale and reproducibility of each pair of runs.

Table 2 lists the raw weight change data and the enthalpies of decomposition. Table 3 lists average weight percentages of residues, condensates and gaseous products as a function of temperature. The amounts of gas phase products, other than condensates, increase from about 0.05 to about 50 wt.% between 473 and 578 K. From 578 to 615 K, the yield of gas products continues to rise to 58 wt.% and then remains constant between 615 and 630 K.

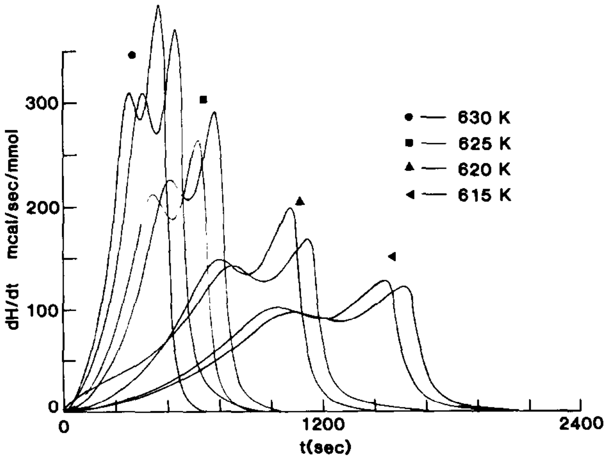

Fig. 1. Baseline corrected plot of dH/dt vs. t.

TABLE 2

Weight changes and enthalpies of decomposition in isothermal calorimetric runs

Run	Temp. (K)	TATB (mg)	Residue		Condensate		Gas (wt.%)	Total time (min)	ΔH (kcal mole^{-1})
			(mg)	(wt.%)	(mg)	(wt.%)			
–	630	3.103	0.920	29.6	0.430	13.8	56.6		
842		3.086	0.937	30.4	0.348	11.3	58.3	19	
843		3.061	0.955	31.2	0.283	9.2	59.6	15	
844		3.089	0.925	29.9	0.281	9.1	61.0	17	
850		3.020	0.982	32.5	0.280	9.3	58.2	14	
851		3.010	0.909	30.2	0.271	9.0	60.8	16	
854		2.999	0.934	31.2				20	−103
855		3.023	0.884	29.2				22	−92
870		3.078	0.947	30.8	0.325	10.6	58.6	21	
871		3.071	0.921	30.0	0.305	9.9	60.1	21	
852	625	3.078	0.967	31.4	0.345	11.2	57.4	23	
853		3.116	0.971	31.2	0.277	8.9	59.9	20	
856		3.105	0.918	29.6				23	−100
857		3.103	0.905	29.2				23	−105
868		3.090	0.977	31.6	0.312	10.1	58.3	26	
869		3.068	0.983	32.0	0.292	9.5	58.5	26	

858	620	3.012	0.905	30.0				30	
859		3.156	1.043	33.0				31	
866		3.082	0.981	31.8	0.235	9.4	58.8	32	
867		3.074	1.070	34.8	0.335	10.9	54.3	32	
860	615	3.052	0.967	31.7				41	
861		3.086	0.920	29.8				42	−99
862		3.084	0.974	31.6				41	−98
863		3.012	1.020	33.9	0.233	7.7	58.4	40	
864		3.096	0.975	31.5	0.345	11.1	57.4	42	
865		3.025	0.967	32.0	0.291	9.6	58.4	41	
993	605	2.975	0.840	28.2			72		−37
994		3.067	0.860	28.2			65		−65
995	600	3.006	0.864	28.7			81		−67
996		3.035	0.927	30.5			90		−64
997	590	3.076	0.831	27.0			175		−39
998		3.024	0.897	29.7			168		−79
991	580	3.055	0.765	25.0			300		−43
999		3.057	1.020	33.4			300		−98
841	578	3.156	0.974	30.9	0.543	17.2	51.9	336	
845		3.062	0.943	30.8	0.544	17.8	51.4	420	

TABLE 3

Average weight percentage variation of decomposition products with temperature

Temperature (K)	Residue (wt.%)	Condensate (wt.%)	Gaseous products (wt.%)
630	31	10	59
625	32	10	58
620	33	10	57
615	32	10	58
578	31	17	52

DISCUSSION

We might expect the isothermal decomposition of TATB to start with an endothermic step, progressing to exothermic steps, with consecutive or concurrent reactions. The vaporization of TATB has an enthalpy, $\Delta H_{\text{vap.}}$, of $\sim$ 43 kcal mole^{-1} [4–6] and it should be an observable endothermic process. Presumably, it is a concurrent and/or participatory step in the thermal decomposition mechanisms. However, there were no detectable endothermic initial steps over the entire temperature range of 528–630 K. The heat produced from exothermic reactions is therefore greater than the heat necessary for vaporization. Figure 1 shows that between 615 and 630 K the unconfined isothermal reactions are complex, with from two to four different exothermic reactions.

Kinetic data treatment: activation energies

The simple thermal decomposition of solids leading to the reaction

$$A_{\text{solid}} \rightarrow B_{\text{solid}} + C_{\text{gas}}$$

proceeds by way of structure-sensitive mechanisms including the nucleation of solid state products, growth of nuclei, and diffusion of gaseous products. The kinetics of heterogeneous solid state reactions have been reviewed and classified by Jacobs and Tompkins [10], Garner [11,12], Keattch and Dollimore [13], Young [14] and Tang and Chaudhri [15]. As a general rule, decomposition of inorganic and metal-organic solids involve nucleation and growth steps [10], while organic solids do not [16]. However, if decomposition takes place in the liquid phase (whether the liquid phase is due to the melting of the solid reactant or to a solution of reactant and products), the reaction becomes a homogeneous one, usually of the first order [17].

We assume that the observed signal is $\mathrm{d}H/\mathrm{d}t = H\ \mathrm{d}\alpha/\mathrm{d}t$, which corresponds to a simple reaction or piecewise to consecutive simple reactions, and

α is the fraction of the reactant that has reacted. This fraction is determined using a running integration of the signal, $\mathrm{d}H/\mathrm{d}t$, vs. time, t, where $\alpha = 0$ at $t = 0$ and $\alpha = 1$ for $\Sigma(\mathrm{d}H/\mathrm{d}t) = H$, when the entire heat of reaction has been liberated. The solid state kinetic rate-laws are all of the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k' \mathrm{f}(\alpha) \tag{1}$$

where k' is the rate constant. The function, $\mathrm{f}(\alpha)$, is either defined by a model of the reaction or is empirically determined. Thus

$$\frac{\mathrm{d}H}{\mathrm{d}t} = k'H \mathrm{f}(\alpha) = k \mathrm{f}(\alpha) \tag{2}$$

since H is a constant at any given temperature. The rate constant, k, is related to the usual one, k', by $k = k'H$.

The curves of α vs. t for all of the data are all sigmoid in form, as is typical for solid state reactions. There is no correlation of the individual curves with temperature, within the range of reproducibility at a given temperature.

The rate-laws derived in the literature are restricted to rather simple reactions. We have not found references to rate-law treatments of consecutive or concurrent reactions in the solid state, although many thermal explosion reactions might be expected to have such complex behavior. Solid state reactions are not homogeneous. They may be dependent on nucleation of products, growth of nuclei and diffusion phenomena; and are, therefore, governed by the rate-laws for such processes. Rogers [17] has emphasized these points with regard to explosives. He also emphasized that unless the rate-law is first-order, or the reactions (or portions of the reactions) are homogeneous, there is no way to treat the data in a physically meaningful or logically consistent fashion. Therefore, he has concentrated on systems that melt with decomposition since liquid phase decomposition is homogeneous. Rogers has also applied the test to organic solids that decompose in the solid state to find which portions of decomposition reactions are first order and/or effectively homogeneous. Since solid state reactions are not truly homogeneous, application of the rate-laws of homogeneous reaction kinetics are not justified theoretically. However, the homogeneous equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = [1 - \alpha]^n \tag{3}$$

can be a good empirical description. Rogers [17] justifies its use on the basis of activated-complex transition-state theory (a semi-empirical theory). He then treats only those portions of the reactions that are first order.

Another, more general approach (but still empirical), is the one which we adopt. We use the library [15] of established heterogenous rate-laws to test the data since, in general, the rate constants for any of these are related to

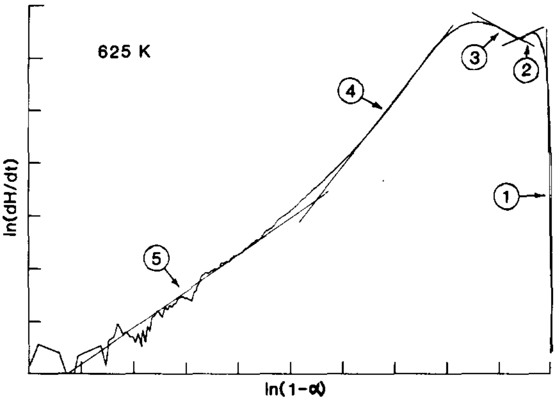

Fig. 2. ln(dH/dt) vs. ln($1-\alpha$). Typical curve, segmenting five distinct regimes.

temperature by an Arrhenius equation [8–18]

$$k' = A' \, e^{E/RT} \text{ and } k = A \, e^{-E/RT} \tag{4}$$

Here, E is to be associated with the activation energy as it is for homogeneous rate-laws. Recently, Rogers and Janney [18] have adopted a somewhat similar approach and have applied it to TATB [19].

Solid state rate-laws have a problem with dimensionality. In homogeneous rate-laws, the activation energy is on a per mole basis. For heterogeneous rate-laws, per mole becomes ambiguous. Activation energies derived from ln k vs. $1/T$ plots will be in units of cal mole^{-1} simply because the gas constant, R, is in units of cal mole^{-1} deg^{-1}. Also, in gas phase, homogeneous chemical kinetics, the A' parameter (pre-exponential factor) is associated via kinetic gas theory to a collision factor. In solid-state kinetics, such an association is not possible.

A practical difficulty is that some experimental data can fit equally well a number of rate-laws. This can lead to derived activation energies that may vary wildly and even be physically meaningless.

These calorimetric data have an additional difficulty. It is clear from Fig. 1, that the two maxima in the dH/dT vs. t curves indicate a complexity not usually treated with established heterogeneous rate-laws. The almost-manageable cases have a single maximum with symmetrical acceleratory and deceleratory stages. Most of the established rate-laws cannot handle both stages with the same parameters [17]. The proper way to handle our data is to deconvolute the curves in Fig. 1 into two separate curves, and test each separately. However, the quality of our data is not sufficient to warrant the effort necessary. Therefore, we treat each curve singly as if it consisted of separate sections, each section of which represents a different reaction stage.

First, we test the calorimetric data shown in Fig. 1 with the general rate-law, eqn. (3), by plotting ln(dH/dt) vs. ln($1-\alpha$). Figure 2 is typical

TABLE 4

Activation energies–unconfined TATB

Stage	Activation energy, ΔE (kcal $mole^{-1}$)	n (order)	Comment
1	62	0.5	Eqn. (7)
	58		Eqn. (8)
	50		Eqn. (8), ref. [19]
2	63	0.27–0.47	Eqn. (5)
	63	0.37	
3	65	0.46–0.55	Eqn. (5)
	56	0.46	
	79		Eqn. (8)
4	50	1.33–1.51	Eqn. (5)
	77	1.38	
5	52	0.55–0.62	Eqn. (5)
	52	0.58	
	50		Eqn. (8)
4–5 *	42, 46	1.0	Recryst. twice from DMSO
4–5 *	57	1.0	Recryst. three times from DMSO
4–5 *	42	1.0	Recryst. three times from DMSO, Al spacers used
4–5 *	49	1.0	Recryst. from diphenyl ether
4–5 *	50	1.0	N^{15} substituted TATB, recryst. from DMSO
4–5 *	49	1.0	H^2 substituted TATB
4–5 *	55	1.0	Old Holston TATB sample

* This data kindly supplied by J. Janney of LASNL.

and represents an order plot of reaction sequences. Five * distinct stages in the reaction are shown in Fig. 2, defined by superposed straight lines.

The slopes of the five straight lines define the orders, n, of the individual reaction stages. The slopes for stages 1 and 3 are negative. A negative n value in eqn. (3) means that $d\alpha/dt$ is decreasing with $(1-\alpha)$. Note, that while $d\alpha/dt$ may decrease, it is physically meaningless for it to become negative. The slopes in stage 1 are very large, within the range of $-18{,}000$ to $-20{,}000$. No attempt was made to extract rate constants, since uncertainties in the order would be reflected as enormous uncertainties in the rate constants. Stage 3, which has a negative slope in the $\ln(dH/dt)$ vs. $\ln(1-\alpha)$ plot, was treated as if the slope were positive. This is equivalent to the prevalent technique of starting at the maximum in the α vs. t curve and working backwards in time for the acceleratory period. (The theoretical

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* The question of whether there are really more than four distinct stages is a matter of point of view. Using Roger's earlier formalism [17], only the portion of the deceleratory region of the data that fits order $n = 1$ would be reduced to give activation energies.

justification for this technique is questionable.) Using each set of data, values of n and of $\ln k$ were obtained for each of the remaining four stages by drawing the four best straight lines. The results of this treatment are included in Table 4. The derived activation energies (50–77 kcal mole^{-1}) are physically reasonable. The values of n are not unity, but range from about 0.3 to 1.5. These values are also physically reasonable in that they are in the same range as that found for many other decompositions. The variation in activation energies calculated for any of the steps is a direct reflection of the precision of the raw data.

Janney [7] used the final deceleratory portion of TATB isothermal calorimetric curves to calculate rate constants and activation energies by forcing a fit to a first-order rate-law (homogeneous, $n = 1$). This was done by using only that portion of the data on the order plot that best fits $n = 1$. As compared with our treatment, the segment of the data that would fit $n = 1$ lies in the transition region between stages 4 and 5 in Fig. 2. Janney's activation energy results on various samples of TATB are listed in Table 4.

The principal objective for testing solid state kinetic data with rate-laws is to try to find a rate-law that accurately describes the α vs. t behavior over the whole reaction range. For simple systems [8–14], it is sometimes possible to fit 90% of the range. When an appropriate rate-law cannot be found, the practice is to segment the reaction into portions that can be fit by individual rate-laws. It is encouraging that four out of five stages in the TATB decomposition could be fit with eqn. (3).

In attempts to obtain better fits, we have plotted the calorimetric data as
(a) $\ln(\mathrm{d}H/\mathrm{d}t)$ vs. $\ln \alpha$;
(b) $\ln[\alpha/(1-\alpha)]$ vs. $\ln t$;
(c) $\ln \alpha$ vs. $\ln t$;
(d) $\ln[\alpha/(1-\alpha)]$ vs. t;
(e) $\ln(1-\alpha)$ vs. t; (f) $\ln \alpha$ vs. t; and
(g) $\ln[-\ln(1-\alpha)]$ vs. $\ln t$.

All of the above correspond to established rate-laws for solid state reactions except for (g) which is empirical, [13] based on generalized rate equations of the form

$$(1-\alpha) = \exp(-kt^n) \qquad (5)$$

Therefore

$$\ln[-\ln(1-\alpha)] = n \ln t - \ln k \qquad (6)$$

Forms (d), (e), and (f) were not useful, since straight lines could not be fitted over major portions of the data. All of the above plots fit the initial, acceleratory portion of the reaction reasonably well. All had difficulty in fitting the final deceleratory portion of the reaction. Of the above fitting procedures, (a) fit stage 1 best, but did very poorly for the remaining stages.

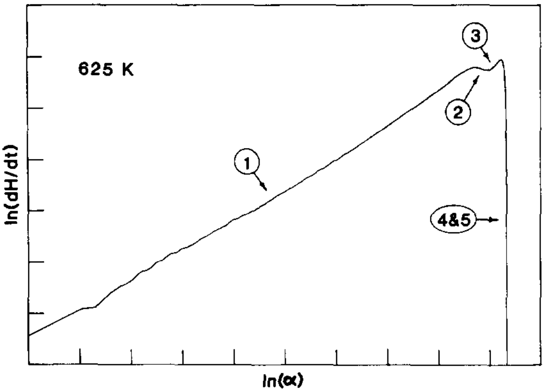

Fig. 3. ln(dH/dt) vs. ln α, eqn. (7). Typical curve, segmenting distinct regimes.

The form of the rate equation from which (a) is derived is

$$\frac{d\alpha}{dt} = k'\alpha^n \tag{7}$$

which is a physically reasonable rate-law for an autocatalytic reaction such as stage 1. An activation energy may be derived from the experimental data using it. Figure 3 is a typical plot of ln(dH/dt) vs. ln α. The five reaction stages segmented in Fig. 2 are identified with the same regions in Fig. 3. The slope of the straight line portion of stage 1 in Fig. 3 is n, and the intercept is ln k. The n values are values in the vicinity of 0.5, and the activation energy is ~ 60 kcal mole^{-1}.

A solid-state rate-law, derived from models of auto-catalytic reactions with branching chain nucleation and interference during growth [15] which we can use to test the data is

$$\frac{d\alpha}{dt} = k'\alpha(1-\alpha) \tag{8}$$

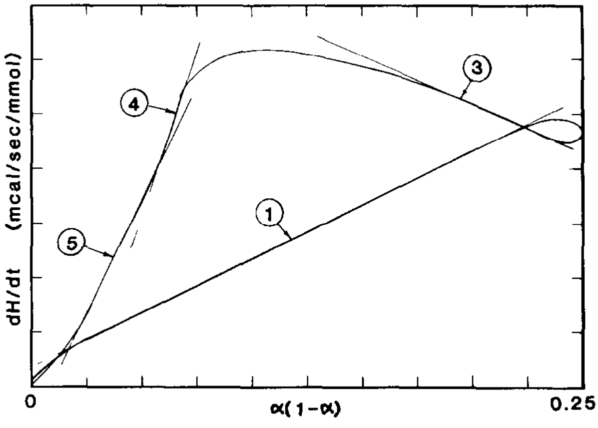

Fig. 4. dH/dt vs. $\alpha(1-\alpha)$, eqn. (8). Typical curve, segmenting distinct regimes.

Figure 4 is a typical plot of $\mathrm{d}H/\mathrm{d}t$ vs. $\alpha(1-\alpha)$. Stages 1, 3, 4 and 5 are shown as straight line segments in Fig. 4. Activation energies for stages 1, 3 and 5 were calculated and are listed in Table 4. Stage 4 was not delineated clearly enough as a straight line segment for all of the runs and so we did not calculate activation energies for this stage. Janney and Rogers [19] have also used eqn. (8) to reduce isothermal calorimetric data from TATB. However, they only treated stage 1. Activation energies from all sources are tabulated in Table 4.

The usual overall objectives for solid state kinetics research are to determine reaction mechanisms using a methodology that attempts to fit the experimentally determined rate data with some rate-law derived from a specific model [10–18]. This technique is unsuccessful since the precision of the data that is necessary to unambiguously assign a specific model is very high even for simple decompositions. Several rate-laws all fit about equally well and as a consequence, the activation energies derived from the same raw data are model (rate-law) dependent and may vary significantly. We concur with Rogers and Janney [18] that, without reactant and product identification information in addition to rate data, chemical reaction mechanisms cannot be determined. Only global kinetics can be obtained. Unconfined TATB decomposition is complex. It is fortuitous that over the small temperature range of 615–630 K, the stages in the reaction mechanisms are so well delineated. Furthermore, in this restricted temperature range, there does not appear to be any indication of mechanism change. The large range of activation energies calculated from the same raw data (Table 4) is not unexpected considering our current state of knowledge and the precision with which these measurements were made. For these data, it is unclear whether the form of the rate-law significantly affects the calculated activation energies.

CONCLUSIONS

For unconfined TATB decompositions from $630 \geq T \geq 575$ K, the isothermal reactions are exothermic. In the range $630 \geq T \geq 615$ K, the reaction consists of perhaps five stages. The first stage is autocatalytic. The activation energy for the first step is 50–60 kcal mole^{-1} and those for the remaining four steps are 50–80 kcal mole^{-1}. The mechanisms for decomposition do not appear to change over this restricted temperature range. There are two types of solid state reaction products; these are a condensate which is similar to TATB, and a residue. We presume that a straightforward, endothermic vaporization of TATB occurs concurrently.

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