

THERMOCHEMICAL DECOMPOSITION OF EXPLOSIVES. I. TNT KINETIC PARAMETERS DETERMINED FROM ESR INVESTIGATIONS

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ABSTRACT

Electron spin resonance techniques have been applied to the thermochemical decomposition kinetics of 2,4,6-trinitrotoluene in the pure liquid state. Direct observation of intermediate and product species in the reaction mixture allowed determination of activation energies which agreed well with previously-determined values utilizing other methods. The autocatalytic nature and complexity of the reaction were demonstrated.

INTRODUCTION

Although studied for over 50 years, the thermochemical decomposition mechanisms of 2,4,6-trinitrotoluene (TNT) and other nitroaromatics are not well understood. The initial decomposition steps have not been clearly identified for either slow decomposition at relatively low temperatures or for conditions at which the thermochemical decomposition reaction is self-sustaining. Because of the widespread military and civilian use of TNT as a secondary explosive, it is increasingly important that its thermochemical decomposition kinetics and mechanism be better understood. This is especially true today in light of the recent development of high-speed military aircraft carrying external ordnance as well as the long-term storage requirements for explosives. In the past, two separate approaches have been used in attempts to elucidate the kinetics and mechanism for this thermochemical decomposition reaction. Several investigators¹⁻⁸ have isolated and identified intermediate products with a view toward elucidation of a stepwise decomposition mechanism. More frequently investigators have determined apparent activation parameters for the overall process and the initial phase by comparison of time-to-explosion data⁹, gas evolution (including weight-loss) data⁹⁻¹³, product analysis data^{5, 6}, or differential scanning calorimetry data^{14, 15} over a range of temperatures. Widespread discrepancies in reported results demonstrate that the process is far from well understood.

In 1921 Robertson⁸ measured a temperature coefficient for the TNT thermochemical decomposition reaction of 1.85 for a 5°C temperature rise. This temperature coefficient was constant over the temperature range 140-180°C. Employing the

Arrhenius equation, one can estimate an average activation energy for the TNT decomposition reaction over the temperature range 140–180°C of 46.0 kcal mole⁻¹. It is important to recognize that these measurements were made during the early stage of the decomposition reaction — commonly referred to as the induction phase of the reaction. In addition Robertson observed a measurable rate of gas evolution after heating TNT at 140°C for 40 h and found the products of the decomposition to be very complex. Using gas evolution methods and measuring the time to explosion, Robertson⁹ found that initially in the decomposition of TNT there was a rapid pressure rise due to partial vaporization of the liquid, followed by a quiescent period during which no gas evolution occurs. This merged into a period of accelerating gas evolution. For the acceleratory phase an activation energy of 34.4 kcal mole⁻¹ was measured. Furthermore, the importance of autocatalysis in the decomposition mechanism was demonstrated by doping a fresh TNT sample with 10% partially decomposed TNT. The quiescent period disappeared and the overall rate increased. Also a number of other additives were found to decrease the induction period and increase the decomposition rate; however, no inhibitors could be found. Using closed ampules where autocatalysis would be greatly facilitated, Roginsky¹⁶ found an activation energy of 27 kcal mole⁻¹. Urbanski and Rychter¹⁷ determined the overall activation energy to be 14 kcal mole⁻¹ at temperatures of 390–450°C. One should note that this temperature range was above the TNT boiling point and thus the value of E_a was affected by the high rate of vaporization. Cook and Abegg¹⁰ followed the TNT decomposition reaction in both the vapor and liquid phases by observing pressure variation. No measurable decomposition of TNT in the vapor phase over the temperature range 250.0–301.0°C was observed. In the liquid phase the induction period activation energy over the temperature range 237.5–276.8°C was determined to be 43.4 ± 0.8 kcal mole⁻¹. Unlike earlier investigators Cook and Abegg¹⁰ were careful to distinguish between the pressure increase due to vaporization and that due to decomposition. Rosen and Dacon¹¹ found that 5 mole% TNT in trinitrobenzene heated isothermally at 230°C produced a small amount of gas at a steady rate. At 240°C a very slowly increasing rate of gas evolution was observed. In addition they postulated that the preferred decomposition process involved an oxidative attack at the methyl group by a nitro group and this probably occurred by both intermolecular and intramolecular reactions. Rauch et al.^{5, 6} concluded that, whereas decomposition is negligible for TNT present only in the gas phase at 275°C, further decomposition of the TNT vapor occurred at this temperature if liquid TNT was present. They measured an activation energy for the acceleratory phase of 34.7 kcal mole⁻¹ and stated that approximately the same value was obtained for the induction period. In testing the effect of additives on the TNT decomposition reaction, Colman and Rauch⁷ found that some free-radical inhibitors when present in large amounts did inhibit the decomposition; however, in general, additives either accelerated the reaction or had no effect on the rate of decomposition. Maksimov and Pavlik¹³ used a Bourdon type compensation manometer to follow gas evolution in the decomposition of TNT over the temperature range 190–270°C. They measured an

activation energy of $34.5 \text{ kcal mole}^{-1}$ for the initial rate of the reaction. For TNT in trinitrobenzene solution Maksimov and Pavlik¹³ found evidence for intramolecular oxidation of the methyl group by an *ortho* nitro group. In the melt, however, both intramolecular and intermolecular interactions appeared to be important.

For explosives, such as TNT, which decompose at a measurable rate only in the liquid phase below the boiling point and which are first order, isothermal differential scanning calorimetry (IDSC) offers a different technique by which to measure kinetic parameters. IDSC measures the rate of energy evolution or absorption by the sample which is directly related to the rate of reaction. Beckmann et al.^{14, 15} successfully employed the IDSC technique to study the thermochemical decomposition of TNT. For the induction phase, they measured an activation energy of $46.5 \pm 1.5 \text{ kcal mole}^{-1}$ while for the post-induction period, they found the activation energy to be $29.4 \pm 1.4 \text{ kcal mole}^{-1}$. The temperature range employed was 245–269°C. By coupling the deuterium isotope effect with the IDSC technique, they were able to show that the rate-determining step in the induction phase of the decomposition of TNT involved a homolytic cleavage of the methyl carbon–hydrogen bond.

Several investigators have taken a different approach in an attempt to obtain a better understanding of mechanism for the thermochemical decomposition of TNT. By isolating and identifying intermediate and final products of the decomposition, they hoped to be able to elucidate a stepwise mechanism for the overall reaction. Adams et al.¹ found that the principal gases found among the decomposition products were nitric oxide, carbon dioxide, carbon monoxide, water and nitrogen. They also found a high-melting toluene-insoluble solid of empirical formula $\text{C}_6\text{H}_3\text{N}_2\text{O}_{3.75}$ and a yellow toluene-soluble solid. Both of these compounds proved to be decomposition catalysts. A possible decomposition route involving an intramolecular oxidation insertion initial step (1-nitroso-4,6-dinitrobenzylalcohol) was proposed. Dacons et al.^{2, 4} heated TNT under air in loosely capped Pyrex tubes at 200°C for 16 h. In analysis of the partial decomposition products by column chromatography, they found at least 25 discrete species as well as large amounts of polymeric material. Principal partial decomposition products that were isolated included 4,6-dinitroanthranil; 2,4,6-trinitrobenzaldehyde; 2,4,6-trinitrobenzyl alcohol; a possible dimeric reduction product of TNT containing a bridging azo or azoxy linkage, two other dimeric reduction products, an oxidation product of TNT and a polymeric material referred to as “explosive coke” which did not melt below 300°C. There was also a very large amount of unconsumed TNT recovered. 1,3,5-trinitrobenzene was conspicuously absent from the partial decomposition products although an exhaustive search for it was made. Using a combined pyrolysis and thin layer chromatographic technique, Rogers³ has investigated the decomposition of TNT between approximately 100 and 370°C. Principal decomposition products found included 1,3,5-trinitrobenzene; 4,6-dinitroanthranil; 2,4,6-trinitrobenzyl alcohol; 2,4,6-trinitrobenzoic acid and an unidentified compound which was probably a dinitro alcohol or aldehyde. Also a large amount of unreacted TNT was recovered. Notably absent was 2,4,6-trinitrobenzaldehyde. Rogers postulated that the initial step in the TNT

decomposition was an oxidative attack on the methyl group with the production of 2,4,6-trinitrobenzyl alcohol. The contrasting findings of the investigations of Rogers³ and Dacons et al.^{2, 4} were believed to be due to an important change in the TNT thermal decomposition pathways with changing reaction medium and/or changing time-temperature history over a relatively narrow temperature span. In their extensive study of Composition B Rauch et al.⁵⁻⁷ studied in some detail the thermochemical decomposition of TNT. For TNT heated at 275°C for 90 min they found essentially the same products as Dacons et al.^{2, 4} as well as the gaseous products N₂, CO₂, CO, NO and H₂O. Furthermore, they noted that only about 1 mole of gas per mole of TNT was evolved. Furthermore, on repeating the work of Dacons et al.^{2, 4}, they not only found the same partial decomposition products as the earlier investigators, but were also able to isolate and identify 1,3,5-trinitrobenzene as well as several other minor products using mass spectral techniques. Based on their overall results and those of other investigators, they proposed a bimolecular oxidative insertion as the initial and probably rate-controlling step.

There are some inherent difficulties with the methods discussed above. Gas evolution studies yield accurate kinetic parameters only if a large amount of gaseous products are evolved during the decomposition reaction. It is well known^{4, 6, 7} that for the thermochemical decomposition of TNT only small amounts of gaseous products (approximately 1 mole gas/mole TNT) are evolved. Thus TNT data based on gas evolution studies are likely to reflect strong inaccuracies. The explosion phenomenon of TNT appears to be strongly governed by the properties and reactivity of the polymeric "explosive coke" rather than by primary processes involving TNT. Because of this, kinetic data based on time-to-explosion studies are suspect.

Isothermal differential scanning calorimetry studies follow the energy evolution or absorption in the decomposition process and thus may be very dependent on several unknown instrumental parameters such as the rate of heat conduction of the sample and reference pans. IDSC kinetic data may be in error unless the effect of these instrumental parameters can be shown to be minimal. Furthermore, for kinetic studies one would ideally like to observe directly the change in concentration of a reactant or product species with time. None of the above methods offer this direct observation. The identification of intermediate and final product species in a reaction as complex as the decomposition of TNT can be very useful when supported with other experimental results. The complexity of the mechanism, however, would preclude drawing definitive mechanistic information from a knowledge of only the intermediate and final products.

A technique which apparently lacks the above drawbacks is electron spin resonance spectroscopy (ESR). If free radicals are produced in the decomposition of TNT, it may be possible to follow directly the change in concentration of a product species with time. Using ESR techniques, Janzen¹⁸ observed spontaneous free-radical formation in the pyrolysis of a number of nitroaromatic compounds including 2,4,6-trinitrotoluene. He found that, if TNT was heated isothermally at 240°C, a concentration of approximately 10^{-4} mole l⁻¹ of free radicals was formed. The ESR thus

offers a new technique by which to study decomposition reactions of nitroaromatic compounds. Furthermore, it does not suffer from any of the drawbacks of earlier techniques and offers the unique advantage of directly measuring the change in concentration of the product species in the reacting melt with time. In addition to obtaining kinetic parameters, one can also obtain product species identification at specific known times during the reaction sequence. This information, coupled with other experimental results, could lead to very reliable mechanistic information.

In this paper we will demonstrate the utility of the ESR technique in obtaining reliable kinetic parameters for the thermochemical decomposition of 2,4,6-trinitrotoluene. Future papers in this series will further investigate the TNT decomposition mechanism both experimentally and theoretically. Experimental work will include dilution studies and product species identification at various points in the reaction. It is anticipated that this technique will lead to a better understanding of the kinetics and mechanisms for the decomposition reactions of a number of important explosives.

EXPERIMENTAL SECTION

All ESR spectra were recorded on Varian 4502 X-band spectrometer utilizing the standard TE_{102} mode rectangular cavity, a modulation frequency of 100 kHz, and a modulation amplitude of 0.5 G. The Varian variable temperature accessory maintained temperatures to within $\pm 0.5^\circ\text{C}$ as measured by a chromel-alumel thermocouple coupled to a Doric Trendicator using a silicon oil sample. This device is accurate to $\pm 1.0^\circ\text{C}$. Temperature gradients were checked both with silicon oil and TNT samples and found to be within $\pm 1^\circ\text{C}$ for the sample volumes used. Within 1 min of their introduction into the ESR cavity, the TNT samples reached a temperature to within 1°C of the stabilized temperature. All decomposition rate data were taken at isothermal conditions with the reported temperature being the average of initial and final temperatures as measured with the silicon oil sample. These initial and final temperatures typically were within 0.5°C of each other. The magnetic field was calibrated by obtaining a spectrum of 2,2-diphenyl-1-picrylhydrazyl in benzene with its well-known g value. Microwave frequencies in the cavity were measured with a Hewlett-Packard 5254M frequency counter with a Hewlett-Packard 5256A frequency converter.

The TNT used for the decomposition was synthesized in this laboratory using standard procedures¹⁹ and purified by recrystallization from ethanol. It was ground to a fine powder and introduced in the standard 3 mm quartz ESR sample tubes. Sample weights of 0.070 g were used for all decomposition rate data except for the mass-dependence studies. For these, sample sizes of 0.040 and 0.100 g were decomposed as well. For selected samples, attempts were made to minimize their exposure to light before decomposition.

A typical TNT decomposition run began by setting a desired temperature on the temperature controller and waiting at least 1 h for conditions to stabilize. The sample was then introduced into the cavity and ESR spectra were taken as often as

necessary to characterize the kinetics of the decomposition. The sample tubes were open to the atmosphere. Relative radical concentrations were monitored by heights of the ESR peaks in the derivative spectra. Care was taken to ensure identical instrument settings and sample conditions in order to accurately measure the relative concentrations.

In order to compare more directly with IDSC data, several experiments were done in which the temperature of the TNT sample was monitored as it underwent decomposition. No ESR spectra were recorded for these runs. These experiments utilized the temperature controller in exactly the same way as those in which ESR data were taken. The thermocouple precluded the possibility of obtaining ESR data while it was immersed in the sample. These data also gave indications of the ability of the temperature controller to maintain a constant temperature during the exothermic decomposition. Short periods of rapid temperature rise (not exceeding 3°C) in the sample at the higher temperatures did occur. This kinetic data obtained during these portions of the experiments were discarded. The temperature range covered was 205–285°C. The times for total decomposition ranged from less than 10 min at the high temperature end of the range to approximately 20 h at the lower temperature end.

RESULTS AND DISCUSSION

Spectral trends

Within a few minutes after sample insertion the heated TNT samples exhibited ESR signals that changed appreciably with time. Figure 1 gives characteristic spectra of the TNT sample at various times into the decomposition at 220°C. The spectra displayed the same trends at all temperatures; only the time required to reach the various phases differed. Early in the decomposition a complicated spectrum with at least 20 lines and splittings of about 2 G appeared. Careful spectra of the wings later in the run showed one additional peak at each end, as shown in the insert of Fig. 1. Figure 1 also gives the numbering system employed to label the peaks. As the run proceeded, all peaks grew, but not necessarily at the same rate. In particular, Peak 11 grew at an accelerating rate throughout the run. Other peaks grew to a point, reached a maximum, and then gradually decreased in intensity. Eventually Peak 11 dominated the spectrum as shown by the last scan of Fig. 1. As can best be determined because of the interference of Peak 11 in the latter stages of the decomposition, all other peaks seemed to follow the same intensity trends, indicating they were due to the same radical; Peak 11, on the other hand, was obviously due to a different radical. At intermediate times it appeared to be the center line of a 1:2:1 triplet which is characteristic of a CH₂-containing radical species. As the decomposition proceeded to completion the side peaks of the triplet coalesced into a single peak. The coalescence occurred as the reaction mixture changed from a liquid to a solid charcoal-like substance and could well have been due to spin-spin exchange between radicals. After decomposition was complete, the single peak did not disappear (remaining for weeks),

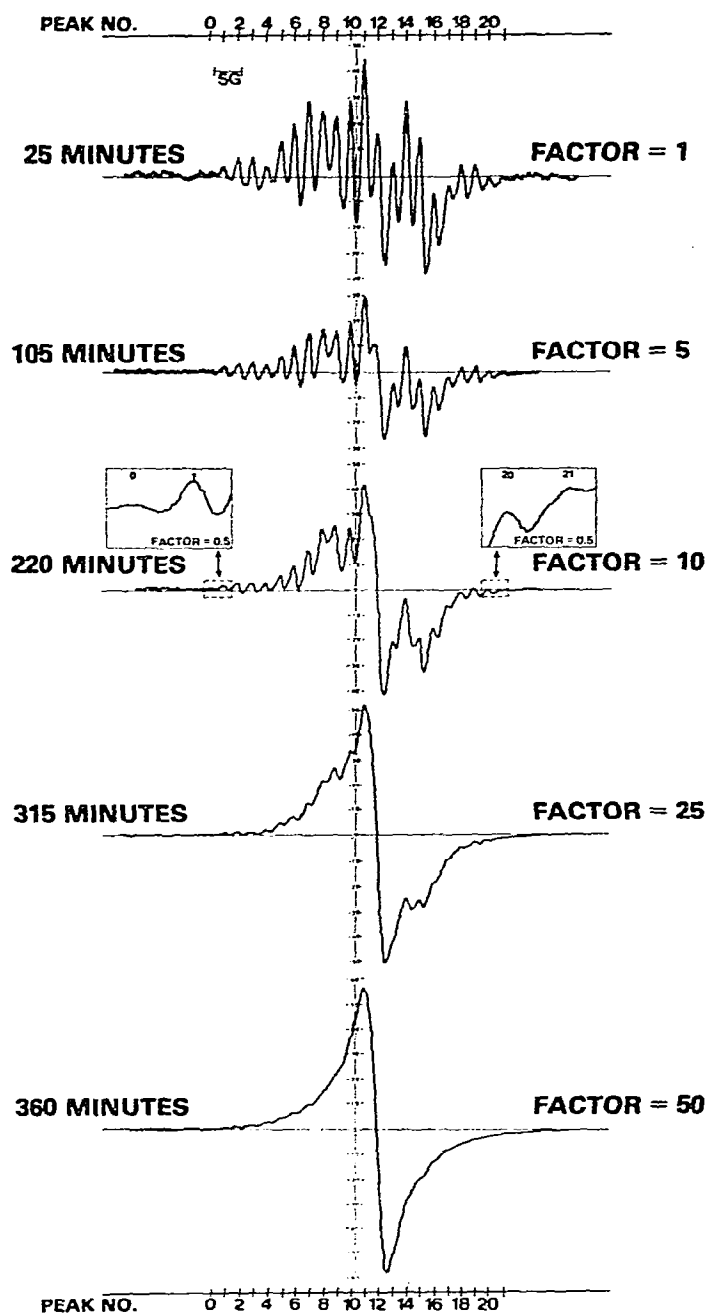


Fig. 1. Time-dependence for the ESR spectrum for the thermochemical decomposition of TNT at 220°C.

even after cooling to room temperature. The appearance of the charcoal-like substance and its persistent ESR spectral characteristics are indicative of polymeric species with permanent radical sites.

The g value of the radical with the complicated spectrum (henceforth called the intermediate radical) was calculated by assuming spectral symmetry and locating the center of its spectrum at the midpoint between the end peaks (Peaks 1 and 20).

Its calculated g value was 2.0044 ± 0.0007 . The g value of the Peak 11 radical (henceforth called the product radical) was calculated to be 2.0017 ± 0.0007 .

Kinetic data

Because of the growth of the product radical peak (Peak 11) throughout the decomposition, its intensity was plotted as a function of time to determine the kinetics of its formation. Figure 2 gives the natural logarithm of its intensity as a function

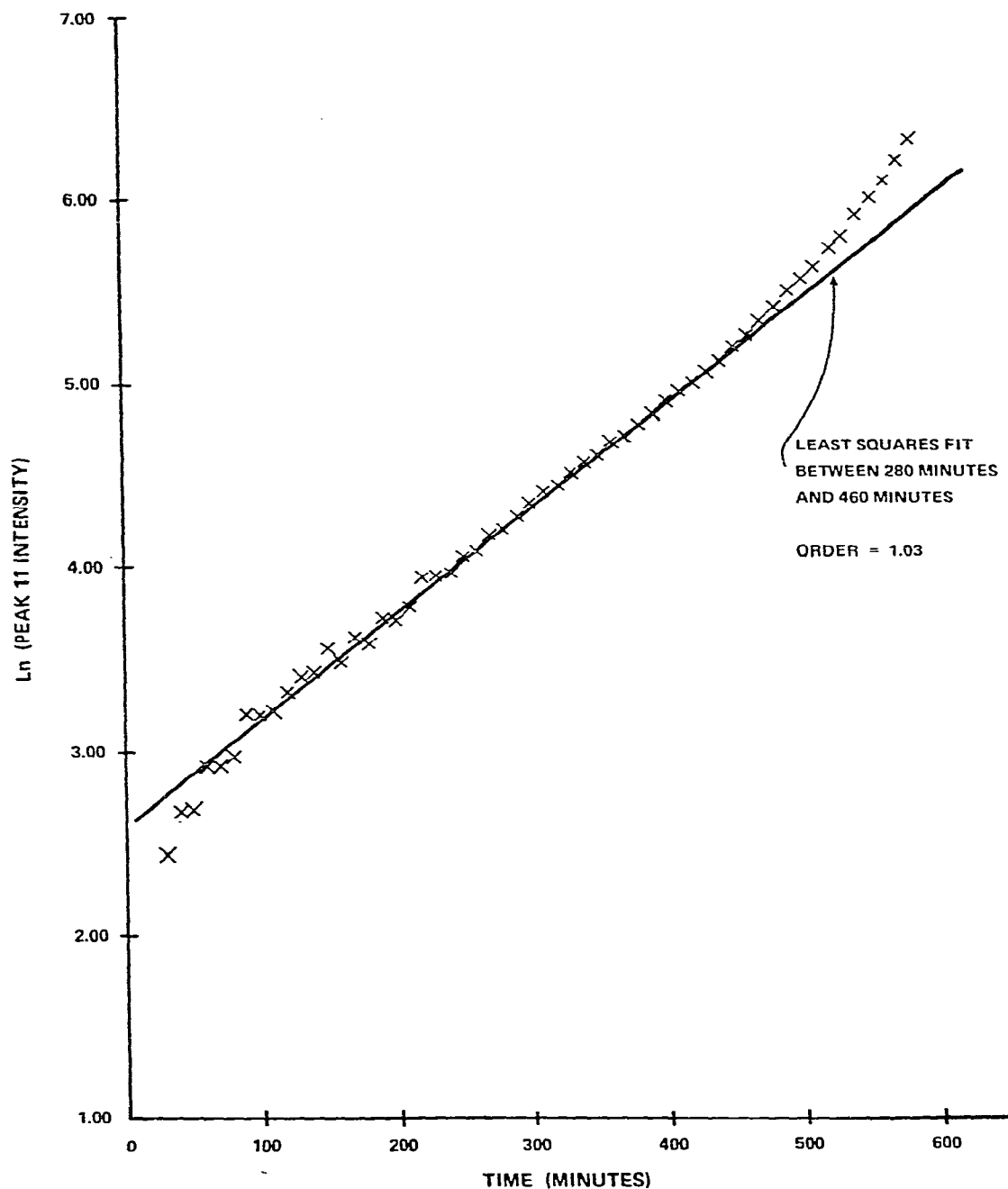


Fig. 2. First order plot of the increase in concentration of the product radical at 215°C.

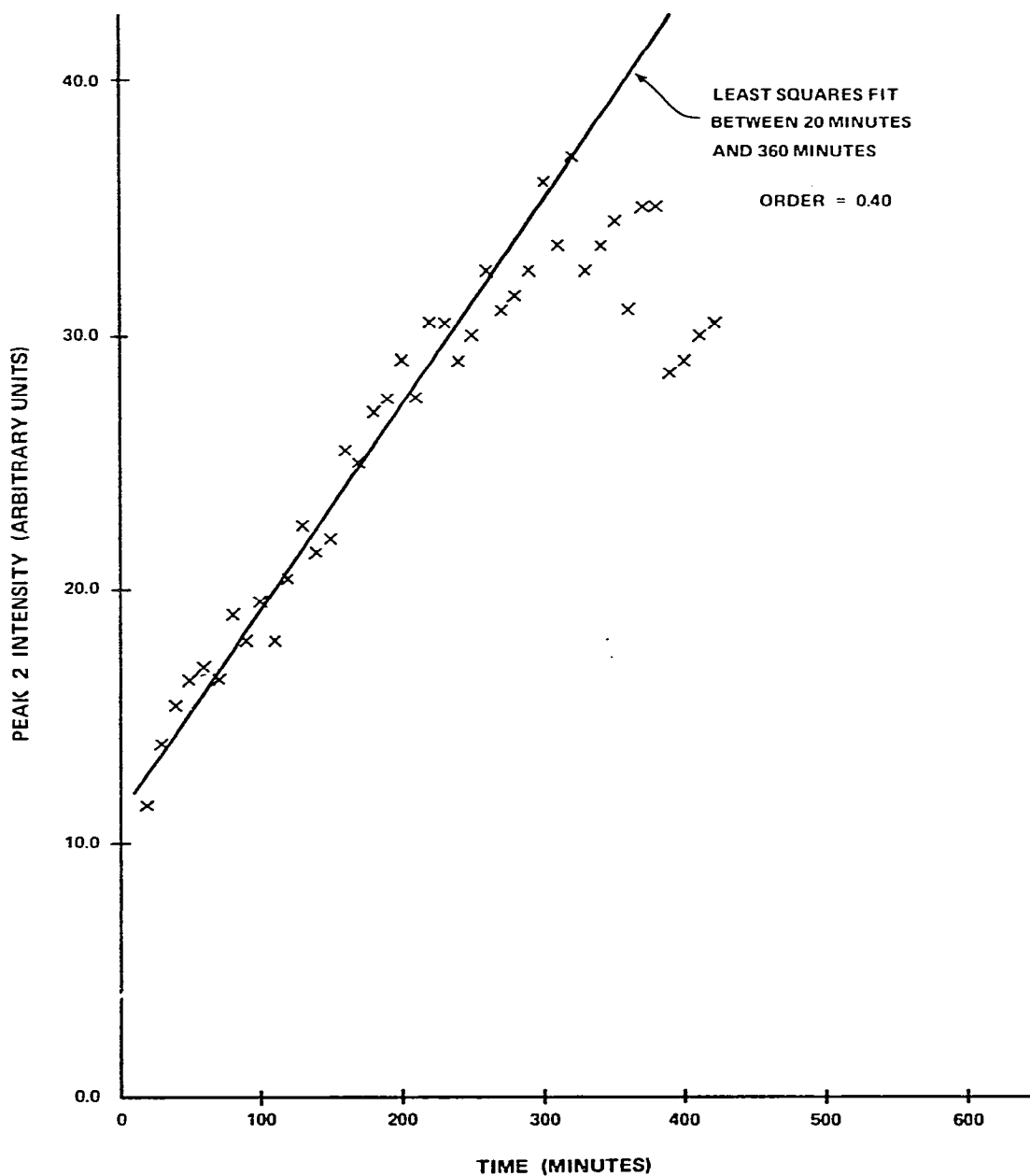


Fig. 3. Zero order plot of the increase in concentration of the intermediate radical at 215°C.

of time for a typical experiment at 215°C. It is evident that there is a considerable portion of the center of the curve which is linear. At very early times the points fall below the line and at later times they deviate upward from the line. The same trends were observed for all temperatures. The order was calculated by plotting $\ln(\Delta I)$ vs. $\ln(I)$ in which I is the intensity. For runs at all temperatures the average order was 1.07 ± 0.12 . Thus it is apparent that the kinetics are first order in the product radical

$$\text{Rate} = \frac{d[\text{P}]}{dt} = k_1 [\text{P}] = k'_1 I \quad (1)$$

in which $[P]$ is the concentration of the product radical. For an ordinary first order reaction, the rate is first order in the reactant, but not the product. This behavior expressed in eqn. (1) indicates some form of autocatalysis in which formation of product enhances formation of more at an increasing rate. Autocatalysis has long been observed by other methods in the liquid-phase thermochemical decomposition^{5-9, 14, 15} of TNT.

It is obvious from the spectra that at least one other radical (the intermediate radical) was produced during the decomposition. Peak 2 was chosen in order to follow the relative concentration of the intermediate radical because of its distance from the product radical peak (Peak 11) in the spectrum. This distance keeps Peak 11 from interfering with Peak 2 until very late in the decomposition. Figure 3 gives a plot of the intensity of Peak 2 vs. time. The plot of intensity vs. time is apparently linear up to a maximum intensity. The order was calculated from $\ln(I/I_0)$ vs. $\ln(t)$ and the average result from runs at all temperatures was -0.08 ± 0.62 . The large uncertainty arose from the data scatter due to the relatively low intensities of Peak 2. Nevertheless, the production of the intermediate radical was apparently zero order over the early part of the decomposition. Beckmann et al.¹⁴ made the assumption of a pseudo-zero order reaction during the early phases of decomposition in order to use the induction time of an IDSC experiment to obtain activation energies. Their interpretation of this induction period involved the slow buildup of a small threshold concentration of some intermediate which then accelerated the main decomposition. This intermediate was assumed to be produced from TNT itself by a reaction of unspecified order: $n\text{TNT} \rightarrow \text{Int} + \text{other products}$, thus

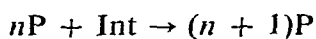
$$\frac{d[\text{Int}]}{dt} = k[\text{TNT}]^n \quad (2)$$

in which Int is the intermediate species. However, if the necessary threshold concentration is small relative to the initial amount of TNT, then $[\text{TNT}]$ will change little during the buildup; the order will have little effect on the reaction rate and the rate will be essentially constant. Our data are consistent with this interpretation of the induction period. Peak 2 appears to be due to an intermediate because of its characteristic initial buildup and then disappearance by the end of the reaction.

Another interesting feature of the plot of the intensity of Peak 2 vs. time was also observed. All experiments gave straight lines, but the intercepts varied by about a factor of three. If this intermediate was formed at constant rate during the early phases of the reaction, then one would expect that the intercept should be zero, since we supposedly started with pure TNT. In addition, at the lower temperatures it was apparent that the first few points fell below the line, but after a short time the points lay on the line and the rate was constant from this time. A possible explanation is that each sample had a small amount of impurity initially present in the TNT which was quickly converted to some non-zero initial concentration of the intermediate radical at the thermochemical decomposition temperatures. This explanation was also supported by one run in which the decomposition was interrupted in the middle

and the sample cooled. At room temperature the product radical peak (Peak 11) was clearly still present but the complicated spectrum of the intermediate radical had disappeared. Upon heating the sample back to decomposition temperatures, the intermediate radical peaks immediately reappeared at the same intensities as when the run was interrupted. Obviously the intermediate radical had been “stored” in some non-radical form upon cooling, since the rate of production of the radical at the decomposition temperature employed would not have allowed an immediate reappearance of the radical at its concentration at the point of interruption. In addition, the variance of the intercepts indicated different amounts of the impurity initially present, perhaps due to varying amounts of exposure to light. There is evidence in the literature that exposure to UV light before decomposition can greatly accelerate the initial stages of the reaction⁹. Attempts to minimize the exposure of selected samples to the lights in the room produced no correlation with the initial radical concentrations.

Returning to Fig. 2, it is interesting to consider the non-first order behavior of the product radical production at early and late phases of the decomposition. During the early phases, several factors may have been responsible. It is quite possible that lines due to the intermediate radical may have contributed to Peak 11 early in the decomposition since Peak 11 was still relatively small. Kinetically, the product radical may have been produced by its reaction with some intermediate that was at a steady-state concentration only during the middle portion of the run. Indeed, the intermediate radical monitored by Peak 2 was near a steady-state condition during approximately the same time period that the first order behavior of the product radical was observed. Both this steady-state assumption and the autocatalytic nature of the production of the final radical can be incorporated into a production step given by



thus

$$\frac{d[\text{P}]}{dt} = k [\text{P}] [\text{Int}]_{\text{ss}} = k_1 [\text{P}] \quad (3)$$

in which P represents a radical site on a polymeric species and Int is some intermediate at a steady-state concentration.

It is tempting to explain the apparent acceleration of the rate of production of the product radical above first order late in the run by coalescence of the 1:2:1 triplet because of spin-spin exchange. This coalescence would have summed all three peaks into the central peak and thus concentrations measured by the height of the central peak would have been too large. However, double integration of the derivative spectra over all three peaks produced an intensity vs. time plot identical with that of the Peak 11 intensity plot. Thus it appears that the acceleration was probably a real kinetic phenomenon. Attempts to fit this acceleration to a simple autocatalytic rate law of $d[\text{P}]/dt = k_1(a - [\text{P}]) + k_2[\text{P}](a - [\text{P}])$, in which a a constant, failed to reproduce the rise in the curve.

Activation energies

In order to determine an activation energy for the first order reaction, the actual rate as measured by $d\ln I/dt$, in which I is the intensity of Peak 11, was set equal to k_1' , the first order rate constant for the production of the product radical (eqn. (1)). Then $\ln k_1'$ was plotted vs. the reciprocal of the absolute temperature as shown in Fig. 4. The slope gives an activation energy of 30.2 ± 0.6 kcal mole⁻¹. This is in good agreement with the activation energy of 29.4 ± 1.4 kcal mole⁻¹ obtained with IDSC

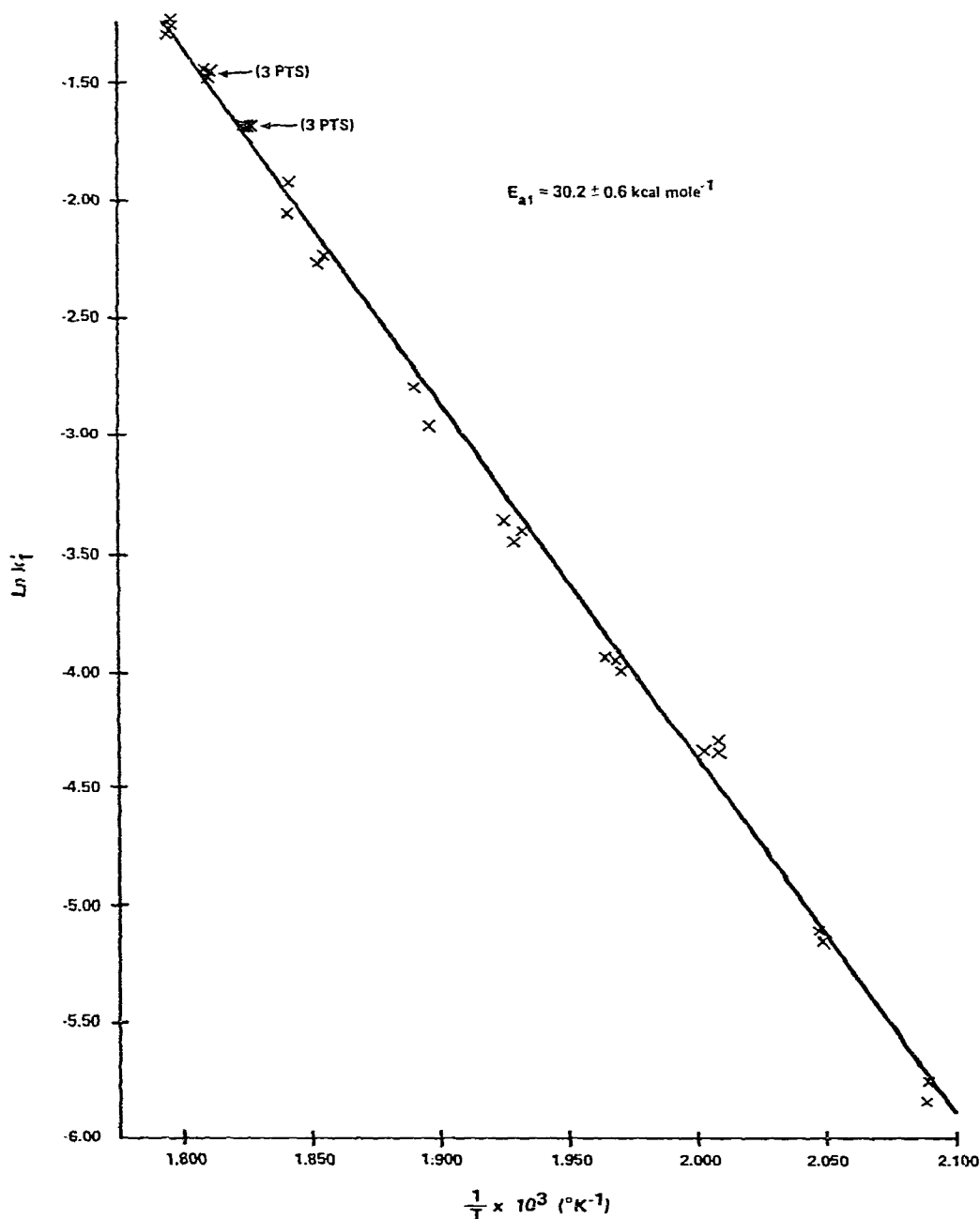


Fig. 4. Arrhenius plot for the production reaction of the product radical.

techniques¹⁴. Similar temperatures over a narrower range were employed in the IDSC studies. The IDSC activation energy was obtained from kinetic data of an exothermic reaction whose rate was decreasing with time during the decay phase. Thus the two could not have been for the same reaction since our rate was increasing

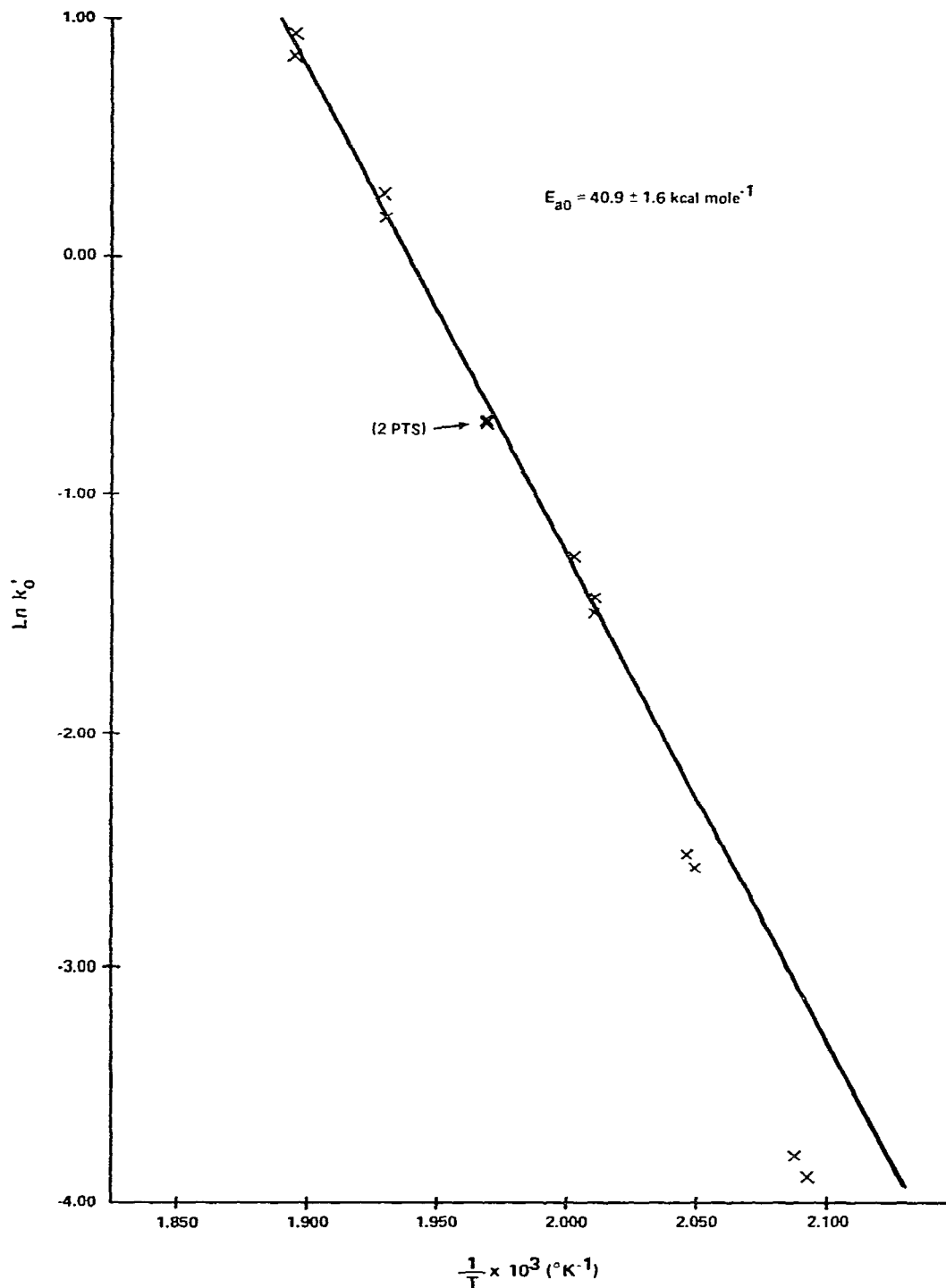


Fig. 5. Arrhenius plot for the production reaction of the intermediate radical.

with time. Therefore it was likely that the two reactions involved were consecutive in nature and both methods were observing the higher activation energy in this portion of the overall scheme.

The rate of appearance of Peak 2 was used to determine an activation energy for the production of the intermediate radical. In this case the natural logarithm of the pseudo-zero order rate constant k'_0 was plotted against the reciprocal of the

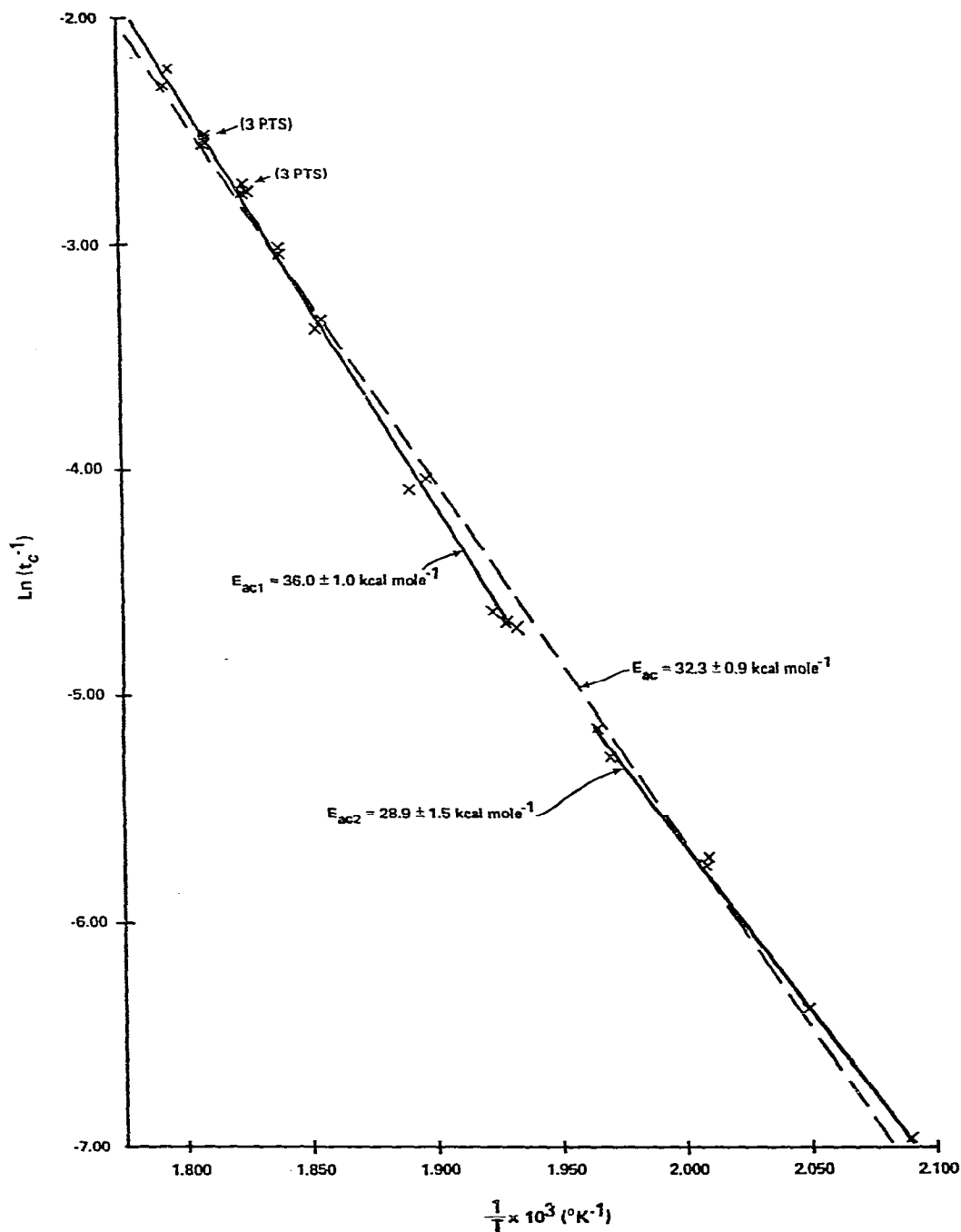


Fig. 6. Arrhenius plot based on the total reaction time.

absolute temperature as shown in Fig. 5. At the highest temperatures the data was distorted due to self-heating of the sample which caused a 3°C temperature rise over a portion of the run. The middle portion of the curve yielded a good straight line from which an activation energy calculated to be 40.9 ± 1.6 kcal mole⁻¹ was obtained. The lowest temperatures clearly fell below the curve and, even though the data are more scattered at these temperatures, this trend is probably not due to data scatter. There is some speculation in the literature of a possible change in mechanism between 200 and 230°C⁴. The value obtained in this study compares favorably with the activation energy of 46.5 ± 1.5 kcal mole⁻¹ obtained from IDSC studies¹⁴ for the induction period. Although the two uncertainties do not overlap, there is some evidence that either the IDSC result is too high (by comparison with d³-TNT)¹⁵ or the uncertainty for the IDSC result is too small²⁰.

Also in the literature is an attempt to obtain an activation energy from the "induction time to explosion"⁹. This time should compare with our time to reaction completion. Taking $(1/t_c)$ as an average rate (t_c being the time to reaction completion) and plotting its natural logarithm vs. the reciprocal temperature we obtain the Arrhenius plot of Fig. 6. There is an apparent curvature to Fig. 6; it has been broken into two parts. Using only the higher temperatures, one obtains an activation energy of 36.0 ± 1.0 kcal mole⁻¹. The lower temperature end of the curve produces a value of 28.9 ± 1.5 kcal mole⁻¹. If one does a least squares fit through all points disregarding the curvature, an activation energy of 32.3 ± 0.9 kcal mole⁻¹ is determined. Even though the last value corresponds well with the previously obtained 32 kcal mole⁻¹ with the same procedure⁹, the curvature of the plot and the differing activation energies demonstrate the danger in using simplifying assumptions of this type. It indicates once again the complicated nature of the reaction.

Mass effects

In order to insure that the decomposition was not mass-dependent, several experiments were run at 235°C with masses of 0.040, 0.070, and 0.100 g, respectively. All gave within 5% of the same rate of decomposition. This is within the normal data scatter. A mass of 0.070 g was chosen as a nominal sample size because it is the smallest amount which fills the effective volume of the ESR sample cavity.

Comparisons with IDSC data

In order to compare with IDSC data previously obtained in this laboratory for the decomposition of TNT^{14, 15} and to ensure that the temperature controller was able to maintain constant temperature, sample temperatures were monitored during decomposition. At the lower temperatures (below 235°C) negligible temperature rises occurred. At the higher temperatures, sample temperatures rose several degrees for short periods of time during the run. Kinetic data during these short temperature rises were discarded. The temperature data near 245°C are compared directly with an averaged IDSC trace at the same temperature in Fig. 7. It is apparent that the ESR sample reached peak temperature before the IDSC trace showed maxi-

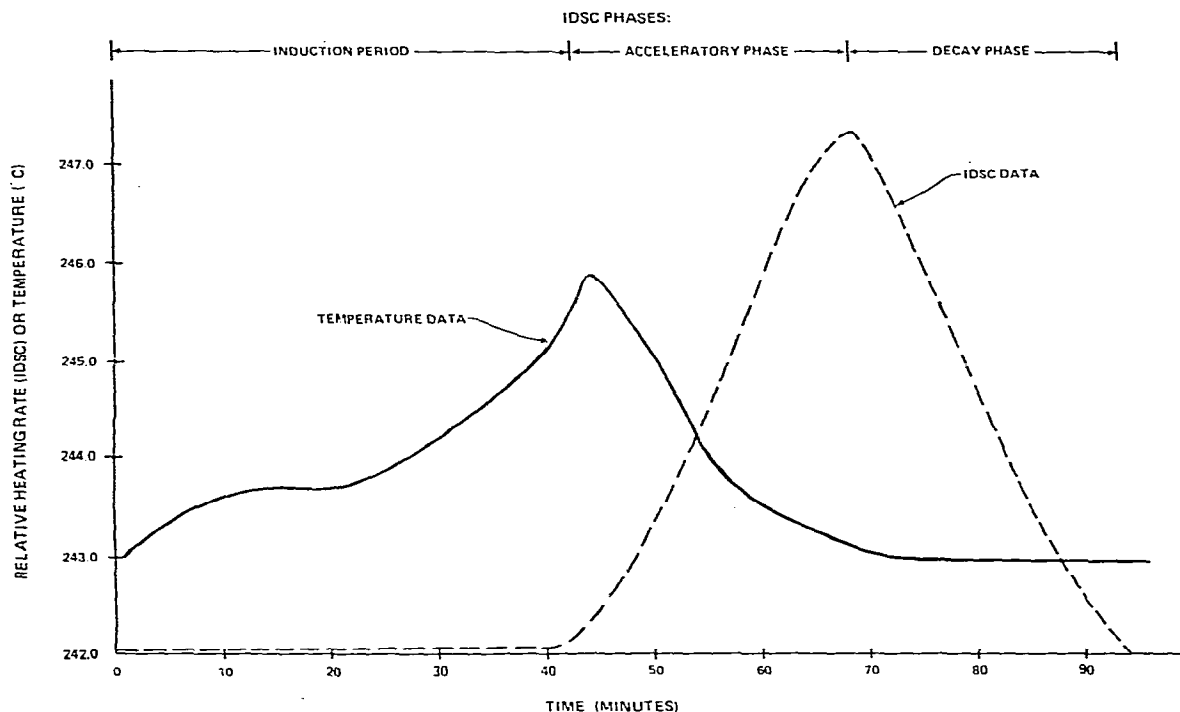


Fig. 7. Comparison of IDSC heating rate vs. temperature fluctuations in ESR sample cell.

imum heat evolution even though the total decomposition times compared very well. The difference between the two could have been due to many factors, such as pressure effects, mass effects, complications from the non-isothermal conditions during the ESR runs or other effects.

CONCLUSION

In this investigation, we have shown the ESR technique to be a viable method for the investigation of the thermochemical decomposition kinetics of explosives. The kinetic parameters successfully obtained for the thermochemical decomposition of TNT are based on the direct observation of the change in species concentration in the reaction mixture. The experimentally determined activation energies of 40.9 ± 1.6 kcal mole⁻¹ for the induction period and 30.2 ± 0.6 kcal mole⁻¹ for the post-induction period agree well with previously reported values determined by other methods. A comparison of liquid-phase TNT thermochemical decomposition kinetic parameters available in the literature is shown in Table I.

In addition, the autocatalytic nature of this thermochemical decomposition reaction has been confirmed. This study also lent strong support to be use of the induction time^{14, 15} for determination of the activation energy of the induction period. A pseudo-zero order initial step and a production step first order in the product species has been demonstrated. Having verified the complexity of the TNT thermochemical decomposition reaction, the dangers of applying simplifying kinetic assumptions to obtain rate constants for the reaction were stressed.

TABLE 1

TNT THERMOCHEMICAL DECOMPOSITION KINETIC PARAMETERS

Investigator(s)	Method ^a	E_a (kcal mole ⁻¹)		Temp. range (°C)
		Induction period	Post-induction period	
R. Robertson ⁸	GE	46.0 ± 3.7		140–180
A. J. B. Robertson ⁹	GE		34.4 ± 2.5	275–310
S. Roginsky ¹⁶	UNK		27 ^b	
T. Urbanski and T. Rychter ¹⁷	UNK		14	390–450
M. Cook and M. Abegg ¹⁰	GE	43.4 ± 0.8		237.5–276.8
F. Rauch and W. Colman ⁶	PA		34.7	235–275
Y. Maksimov ¹³	GE	34.5 ^c		190–270
J. Beckmann et al. ¹⁴	IDSC	46.5 ± 1.5	29.4 ± 1.4	245–269
This study	ESR	40.9 ± 1.6	30.2 ± 0.6	205–285

^a UNK = unknown, GE = gas evolution (weight loss) studies, PA = product analysis studies, IDSC = isothermal differential scanning calorimetry, ESR = electron spin resonance techniques.

^b Period of reaction unknown, but magnitude of E_a suggests post-induction period.

^c Initial rate data employed although contributions from later phases of the reaction seem likely.

In the future, experimental studies will attempt to deduce the radical identities and correlate product formation with the ESR spectra. Furthermore, concentration studies using an inert solvent will be done to determine the molecularity of the initial step. Current theoretical work using the MNDO computer program to calculate kinetic parameters for probable reaction mechanisms will continue.

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