DIFFERENTIAL SCANNING CALORIMETRIC DETERMINATION OF KINETICS CONSTANTS OF SYSTEMS THAT MELT WITH DECOMPOSITION

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ABSTRACT

Methods for the detection of systems that melt with decomposition are discussed, and a differential scanning calorimetric (DSC) method is presented for the determination of the kinetics constants of such systems. It is now possible to specify characteristics of kinetics curves corresponding to decomposition in the solid phase, the mixed solid and liquid phases, or the homogeneous liquid phase. The method is illustrated by application to cupferron tosylate and HMX.

INTRODUCTION

Many organic decomposition reactions have been analyzed as solid-state reactions, with various nucleation-growth or autocatalysis models being used for the interpretation of experimental rate data. These treatments attempt to linearize sigmoid reaction data over as large a reaction span as possible to obtain "rate constants." One recent example of the approach was published by Dorko, Hughes, and Downs[1], who assumed a solid-state reaction because it "... becomes obvious that as the decomposition occurs at temperatures substantially below the melting point, effects other than chemical or melting begin to play substantial roles in determining the reaction mechanism." Sigmoid reaction curves do not always denote chemical autocatalysis or nucleation-growth processes[1,2]; they also can be produced by systems that melt with decomposition[3]. The linearization of the data from a system that melts with decomposition gives a "rate constant" that is devoid of any chemical significance.

The most obvious characteristic of the decomposition of a high-melting organic compound below its melting point is that its initial rate is essentially zero, *i.e.*, there is an induction time. The initial rate of a homogeneous reaction is the highest rate. A change from a rate curve with an induction time to a normal rate curve across the nominal melting point of a compound defines a system that melts with decomposition. Any compound that melts with decomposition and shows a variation in melting point with heating rate in a capillary apparatus should be suspect, and considerable confusion could have been avoided in the literature by visual observation.

Many measurements have been made on systems involving mixed phases;

therefore, rates of melting, as well as rates of decomposition in the two phases, have affected the results. Rates of melting increase very rapidly with increases in temperature, and organic compounds normally decompose more rapidly in the melt; therefore, many organic systems can show very high apparent activation energies and pre-exponentials[4,5]. Manelis and Dubovitskii[6] presented a theoretical discussion of systems that melt with decomposition; however, in the absence of solubility data, rate measurements must be made on a single, known phase to yield data that can be analyzed.

Robertson[7] published kinetics constants for the decomposition of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), pointing out that it melted with decomposition. Dorko et al.[1] published data on the decomposition of cupferron tosylate (N-phenyl-N'-tosyloxydiimide N-oxide), using solid-state models for the analysis of the data. Therefore, HMX and cupferron tosylate have been used in the present work to illustrate the problems associated with such systems.

EXPERIMENTAL

Apparatus. — All measurements were made with a Perkin–Elmer Model DSC-1B differential scanning calorimeter. Samples were sealed in aluminum cells, Perkin–Elmer Part Number 219-0062, and the cells were perforated with a single hole approximately 0.15 mm in diameter.

Samples. — The sample of cupferron tosylate was prepared and purified by M. D. Coburn of this Laboratory. The HMX sample was recrystallized from a filtered acetone solution of 99.9% pure HMX, provided by the United Kingdom Atomic Energy Research Establishment, Aldermaston.

Procedure. — It is important to calibrate both the average and differential temperature settings of the instrument as accurately as possible before making isothermal measurements. The differential temperature settings should be made as close to the temperature of the measurement as possible, because the two supports do not maintain identical temperatures throughout the entire span of the instrument. Temperature errors of several degrees can be observed if the differential temperature calibration is not properly made.

In making a measurement, the instrument and recorder zero are set at the test temperature with two empty cells on the supports. The cell on the sample support is removed, and the instrument is allowed to equilibrate. The recorder is started, the instrument range switch is set on the desired range, and the sample is dropped onto the sample support. The sharp break on the record is used to mark zero time; however, the absolute position of the zero point on the time axis is unimportant for the determination of rate constants, because the rate constant is determined from the slope of the ln deflection (*b*) *versus* time (*t*) plot.

The fraction decomposed (*x*) is determined by integration of the curve[1]; however, the integrations in this work were accomplished by use of Simpson's Rule and a computer.
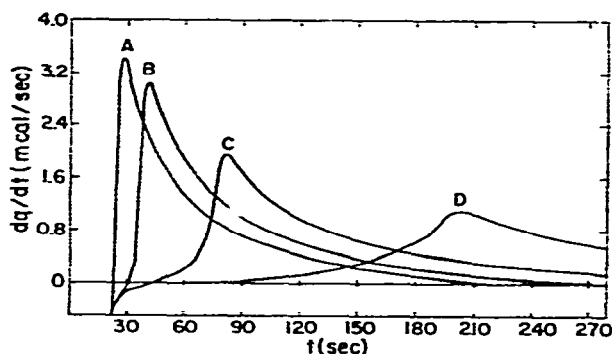
Fig. 1. Representative isothermal rate curves for cupferron tosylate. A, 410°K (above the nominal melting point); B, 407.5°K (just below the nominal melting point); C, 405°K; D, 400°K.

RESULTS

Fig. 1 shows a representative set of isothermal rate curves for cupferron tosylate, taken above and below the nominal melting point. The observed capillary melting point is a function of the heating rate, but the nominal melting point is approximately 409–410°K. It can be seen that an induction time appears at temperatures below the melting point, with a duration that increases as the temperature is lowered; however, the late part of each curve has the characteristics of a normal rate curve. When the rate curves are converted into reaction history curves (plots of residual fraction, $1 - x$, *versus* time), it can be seen that the curve is sigmoid below the melting point but normal above the melting point (Fig. 2).
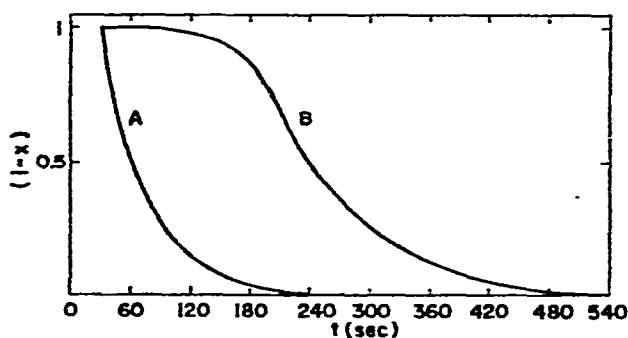

Fig. 2. Reaction history curves for cupferron tosylate above and below the nominal melting point. The 30 sec delay is caused by the time required for instrument equilibration. A, 410°K; B, 400°K.

Fig. 3 shows a series of programmed-temperature curves for the tosylate. The curves have been reduced to the same temperature scale, but they have different time scales; all of the curves would have approximately the same deflection–time integral. The melting point is seen only at high programming rates, a criterion used by Dus-
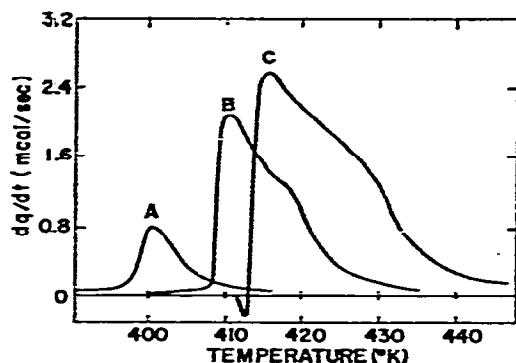
Fig. 3. Programmed-temperature DSC curves for cupferron tosylate at different heating rates. A, 2.5°/min; B, 10°/min; C, 20°/min.

walt[8] to detect systems that melt with decomposition. This observation is in agreement with the fact that the measured capillary melting point is a function of heating rate.
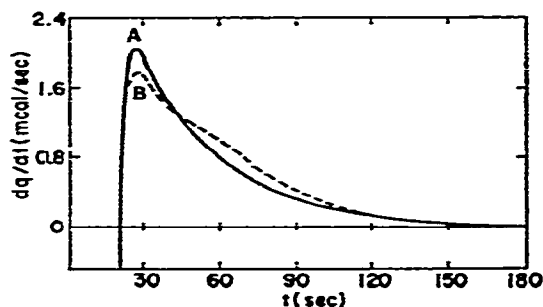

Fig. 4. Isothermal rate curves for cupferron tosylate at 415°K. A, perforated cell; B, sealed cell. The average heat of reaction in a perforated cell is 236 cal/g; in a sealed cell it is 320 cal/g.

Sealed DSC cells were used to make the curves shown in Fig. 3, and an unresolved series reaction can be seen in the later portions of the curves. Fig. 4 shows that the secondary reaction is reduced when isothermal measurements are made in perforated sample cells. First-order plots of isothermal runs, made in sealed and perforated cells, above and below the melting point of the tosylate are shown in Fig. 5. The complexity of the reaction in the sealed cell can be detected, and it is easy to see the portion of the decomposition in a perforated cell that can be used for measurement. The degree of complexity of the tosylate decomposition is not severe, making it excellent for purposes of illustration.

Manelis and Dubovitskii[6] showed what the characteristics of a system that melts with decomposition should be. They considered systems with and without additional autocatalysis and inert impurities, but they assumed that the decomposition in the solid followed a first-order law, a very unlikely situation. However, most organic
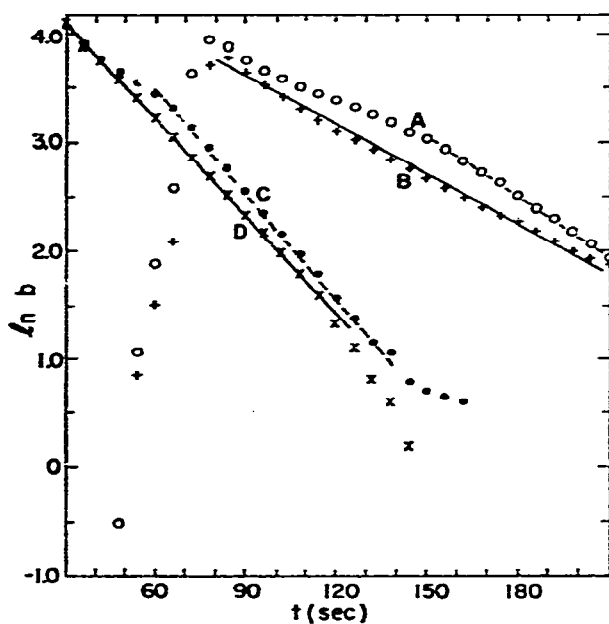
Fig. 5. First-order plots of isothermal data obtained with sealed and perforated cells above and below the nominal melting point of cupferron tosylate. A, sealed cell at 405°K; B, perforated cell at 405°K; C, sealed cell at 415°K; D, perforated cell at 415°K.

compounds decompose so much more rapidly in the melt than in the solid that assumptions about the solid are not critical. They indicate that systems that decompose
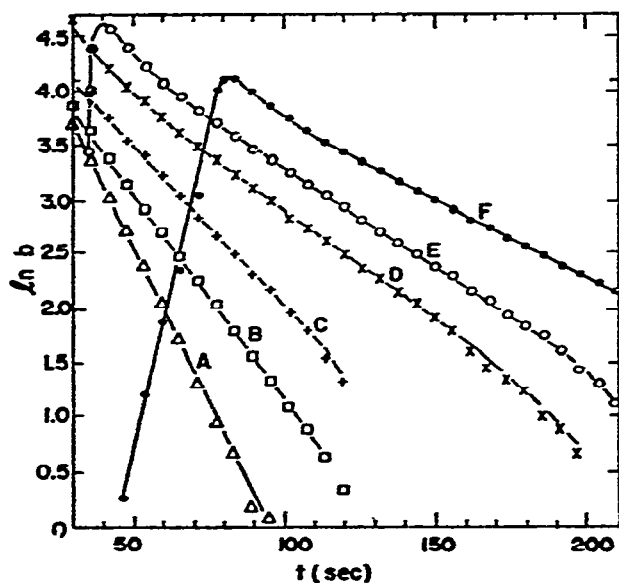

Fig. 6. Representative first-order plots of isothermal data for the decomposition of cupferron tosylate. A, 425°K, $k = 0.0560 \, \text{sec}^{-1}$; B, 420°K, $k = 0.0412 \, \text{sec}^{-1}$; C, 415°K, $k = 0.0295 \, \text{sec}^{-1}$; D, 410°K, $k = 0.0210 \, \text{sec}^{-1}$; E, 407.5°K, $k = 0.0181 \, \text{sec}^{-1}$; F, 405°K, $k = 0.0145 \, \text{sec}^{-1}$;

more rapidly in the liquid than in the solid without autocatalysis (a situation that can be demonstrated experimentally for any specific compound) have the following important characteristic: "The maximum rate is reached ... at the point where dissolution is complete." This fact makes it possible to analyze decomposition data to determine rate constants; the part of the curve that results from decomposition in a homogeneous liquid phase can be specified.

Some representative first-order plots for the decomposition of cupferron tosylate are shown in Fig. 6. It can be seen that linear plots are obtained for data past the maximum rate, i.e., through the portion of the curves known to be the result of decomposition in a homogeneous liquid phase. The data can be analyzed with confidence, and the activation energy, E, and pre-exponential, Z, can be determined.
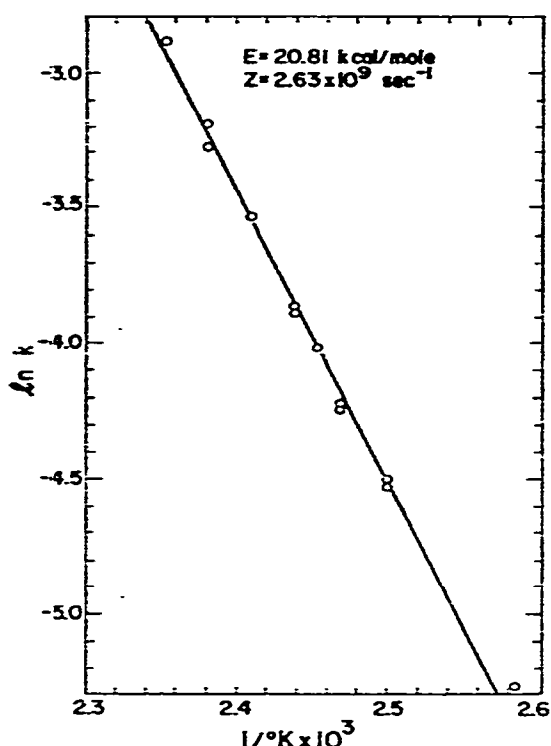

Fig. 7. Arrhenius plot of all isothermal data obtained on cupferron tosylate with perforated cells.

The Arrhenius plot of all of the cupferron tosylate rate constants is shown in Fig. 7. The Arrhenius plot shows that there is no discontinuity in the rate data across the nominal melting point of the compound. This is because the data were obtained after the maximum rate; all represent rates of decomposition in a homogeneous liquid phase. Maksimov[5] showed that there is a very large discontinuity in apparent rate constants across a phase transition. The linearity of this Arrhenius plot across the nominal melting point of the compound proves that the often unrecognized fact that organic compounds melt with decomposition at temperatures well below their

nominal melting points must be accepted, and can be proved, for any specific compound.

Dorko *et al.*[1], using perforated cells, analyzed the data for cupferron tosylate with an autocatalytic model. Fig. 4 and Fig. 5 show that there is little effect of gaseous products, and Fig. 8 shows the effect of the addition of condensed decomposition products of the reaction to fresh reactant. The impurity eliminates the induction time,
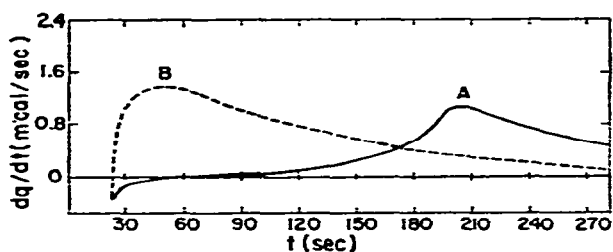

Fig. 8. Comparison of rate curves for cupferron tosylate at 400°K with and without addition of condensed decomposition products. A, Pure tosylate in perforated cell; B, tosylate with 26.1% decomposition products added in perforated cell.

i.e., it produces an immediate liquid phase at 400°K. Fig. 9 shows first-order plots of the data from Fig. 8; the rate constants obtained from the two curves are identical,
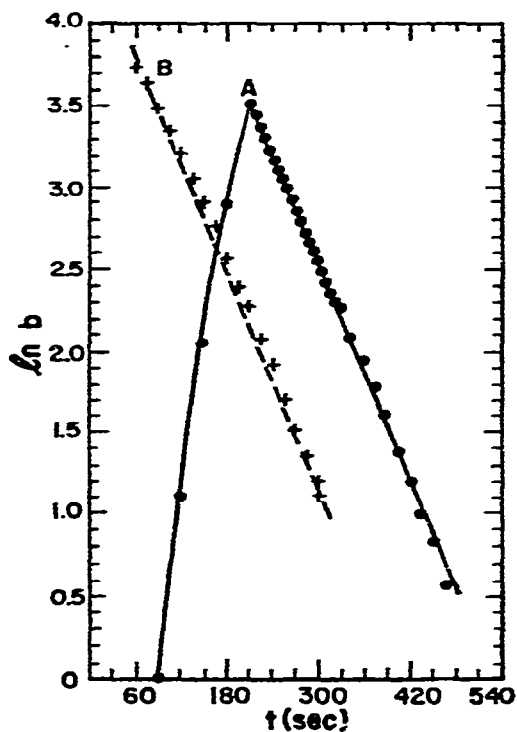

Fig. 9. First-order plots of data from Fig. 8. A, pure tosylate, $k = 0.0108$ sec^{-1}; B, 26.1% decomposition products added, $k = 0.0106$ sec^{-1}.

and there is no evidence of autocatalysis caused by the condensed products. All of the characteristics of the reaction can be explained by melting-with-decomposition, as described by Bawn[3].

It has been shown that a decomposition in a homogeneous liquid phase must be first order[9,10], unless the reaction is complex. If the reaction is complex, meaningful rate constants cannot be obtained. Therefore, it is important to determine the order and complexity of a reaction while the data are being analyzed. A linear first-order plot indicates a well-behaved reaction, but an excellent method for the determination of order and complexity for isothermal decompositions is the production of an "order plot." A simple reaction should follow an expression such as

$$dx/dt = k(1-x)^n \tag{1}$$

where n is the reaction order and k is the rate constant. However, using a DSC, the rate of the reaction is proportional to the DSC deflection from the baseline, b. Therefore

$$\alpha b = dx/dt = k(1-x)^n \tag{2}$$

where α is a proportionality constant. It follows that
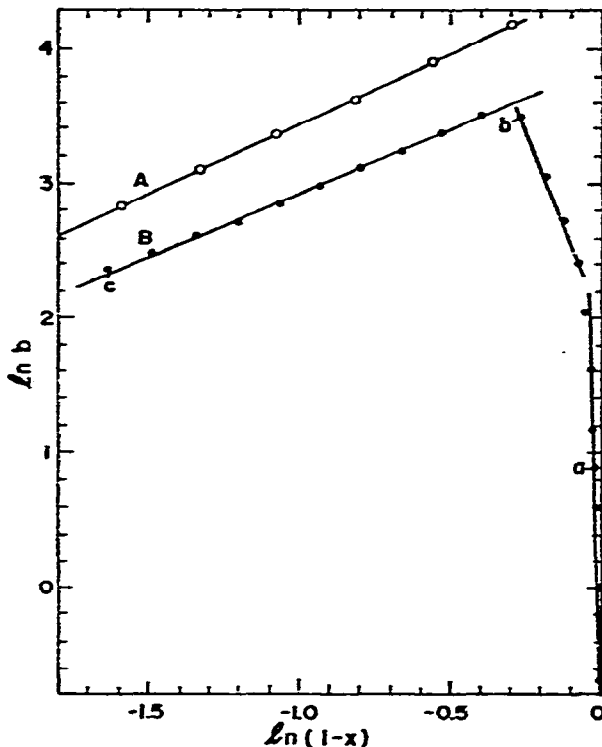
$$\ln b = n \ln(1-x) + C \tag{3}$$

Fig. 10. Order plots for the decomposition of cupferron tosylate at temperatures above and below its nominal melting point. A, 410°K, $n = 0.99$; B, 400°K, $n = 0.92$. a, 1.2% decomposition, probably solid phase, $n \rightarrow -\infty$; b, 23% decomposition, end of melting, $n = -6.5$; c, 80.4% decomposition.

where C is a constant. Therefore, a plot of ln b *versus* ln$(1-x)$ should give a straight line with a slope equal to the reaction order. A curved or discontinuous plot indicates complexity. A comparison of order plots for cupferron tosylate at temperatures above and below the melting point is shown in Fig. 10. The reaction past the curve maximum is simple, *i.e.*, the line is straight and the order is one. It can be seen that the early part of the reaction below the melting point is not simple; relatively large negative orders are obtained. A negative order indicates that the rate is increasing as the amount of reactant is decreasing. Nucleation-growth and autocatalytic systems both show this behavior. In melting-with-decomposition, an early solid-state reaction must proceed during the induction time, producing the products that lead to the formation of a melt. If this solid-state process has the general characteristics of a nucleation-growth process, it could have a very high negative order. Such a phase of reaction can be observed in a melting-with-decomposition order plot. Once the system has started to melt, the rate will increase as the absolute amount of melt increases, up to the instant of complete melting. The apparent order of this phase of the reaction will depend on the difference in rate between the solid and liquid decompositions. The melting-with-decomposition part of the reaction will normally show a relatively low negative order. Dorko *et al.*[1] stated that "... the early stages of the reaction can be analyzed as a simple first-order reaction." It is the early stage of the reaction that *cannot* be analyzed as a first-order reaction.
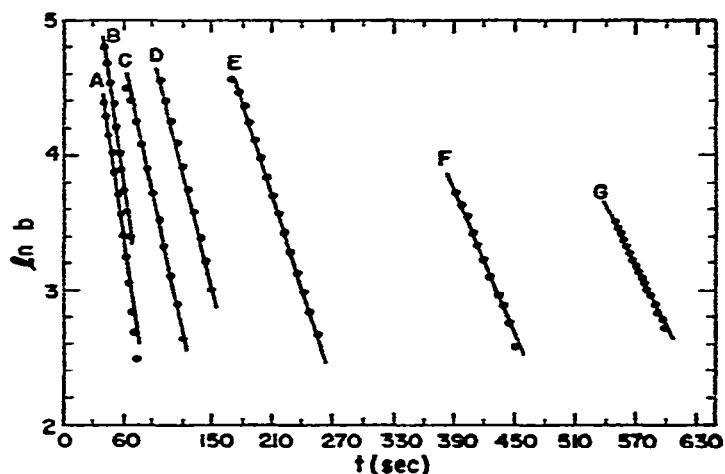

Fig. 11. First-order plots for the decomposition of HMX in the homogeneous liquid phase. A, 558°K, $k = 0.050$ sec^{-1}; B, 558°K, $k = 0.052$ sec^{-1}; C, 552°K, $k = 0.032$ sec^{-1}; D, 550°K, $k = 0.028$ sec^{-1}; E, 548°K, $k = 0.023$ sec^{-1}; F, 546°K, $k = 0.018$ sec^{-1}; G, 544°K, $k = 0.015$ sec^{-1}.

In order to establish more clearly the characteristics of systems that melt with decomposition, a well known system[7], HMX, was studied by isothermal DSC. A series of first-order plots for HMK is shown in Fig. 11. Only data from the decomposition in the homogeneous liquid phase are plotted. Order plots above and below
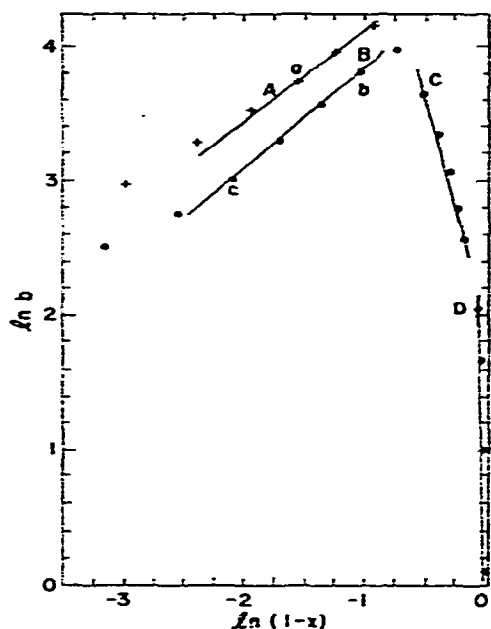
Fig. 12. Order plots for the decomposition of HMX at temperatures above and below the nominal melting point. A, 554°K (slightly above the melting point), $n = 0.7$; a, 80% decomposition. B, 546°K (well below the nominal melting point), $n = 0.7$; b, 64% decomposition, c, 88% decomposition. C, Melting-with-decomposition at 546°K, $n = -3.3$. D, Solid-state stage of decomposition at 546°K, $n \rightarrow -\infty$.

the melting point are shown in Fig. 12. An obvious early solid-state stage can be detected in the reaction below the melting point; however, it should be pointed out that the duration and extent of this early stage are very erratic, depending on the purity and perfection of the specific sample taken. The Arrhenius plot of the HMX
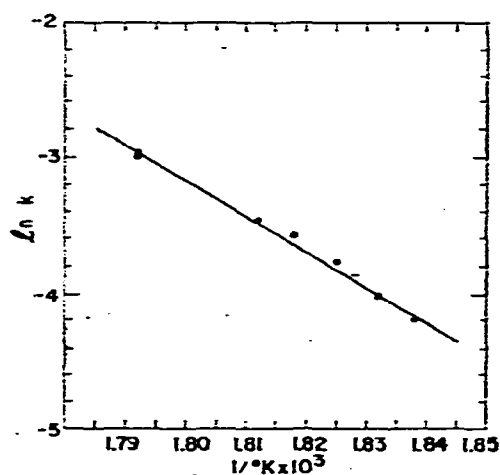

Fig. 13. Arrhenius plot of isothermal decomposition data for HMX in the homogeneous liquid phase; $E = 51.3$ kcal/mole, $Z = 6.4 \times 10^{18}$ sec^{-1}.

data is shown in Fig. 13. Again there is no discontinuity across the nominal melting point (approximately 280°C). The activation energy, E, of 51.3 kcal/mole and pre-exponential, Z, of 6.4×10^{18} sec^{-1} agree extremely well with Robertson's results[7] ($E = 52.7 \pm 2$ kcal/mole and $Z = 5 \times 10^{19}$ sec^{-1}) and programmed-temperature DSC results[4,11] ($E = 50.3$ kcal/mole and $Z = 1.26 \times 10^{18}$ sec^{-1}). Sample purity had a negligible effect on reaction rate; samples between 93 and 99.9% pure all showed rate constants between 0.018 and 0.022 sec^{-1} at 546°K.

CONCLUSIONS

Systems that melt with decomposition can be detected as follows: (a) the capillary melting point is a function of heating rate; (b) the size of the DTA or DSC melting endotherm is a function of the heating rate; and (c) decomposition rate curves show an induction time at temperatures below the nominal melting point.

No attempt should be made to linearize all of the data for a system that melts with decomposition for the determination of rate constants. In the absence of auto-catalysis, melting will end and a homogeneous liquid phase will be produced at the instant the maximum rate is attained. Only data past the curve maximum should be analyzed for the determination of rate constants.

ACKNOWLEDGMENT

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