Thermal Decomposition Process of HMX

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Der thermische Zersetzungsprozeß bei HMX

Die thermische Zersetzung von HMX wurde untersucht oberhalb und unterhalb seines Schmelzpunktes unter Einsatz der Thermoanalytik und der Infrarotspektroskopie. Der Gewichtsverlust, der auftritt, wenn die Temperatur mit konstanter Geschwindigkeit erhöht wird, läßt sich vier Elementarprozessen zuordnen: Induktionsperiode, Sublimation, Festphasenreaktion 1. Ordnung und stark exotherme Flüssigphasenreaktion; diese wurden graphisch dargestellt durch Auftragen des Logarithmus der Aufheizgeschwindigkeit gegen die reziproke Temperatur. Hydroxymethylformamid wurde als Hauptprodukt bei der Zersetzung in der flüssigen Phase nachgewiesen; damit wird nahegelegt, daß die Zersetzung des HMX in der flüssigen Phase eingeleitet wird durch die Aufspaltung der N-N Bindung und nicht der C-N Bindung.

La décomposition thermique de l'octogène

On a étudié, par thermo-analyse et par spectroscopie infrarouge, la décomposition thermique de l'octogène aux températures inférieures et supérieures à son point de fusion. La perte de masse que l'on observe quand la température croît de manière constante, peut être rapportée à quatre processus élémentaires parfaitement distincts: la période initiale, la sublimation, la réaction de 1er ordre en phase solide et la réaction fortement exothermique en phase liquide. Ces différents processus ont pu être décelés graphiquement en enregistrant le logarithme de la vitesse d'échauffement en fonction de l'inverse de la température. Lors de la décomposition en phase liquide, il se forme surtout de l'hydroxyméthylformamide, ce qui laisse supposer que la décomposition de l'octogène en phase liquide débute par l'ouverture de la liaison N-N et non par celle de la liaison C-N.

Summary

The thermal decomposition of HMX has been investigated using thermoanalytical techniques and infrared spectroscopic study at both above and below its melting point. The weight loss phenomenon that occurs as the temperature is elevated at a constant heating rate has been clearly separated into four elementary processes which are induction period, sublimation, first order solid phase reaction, and highly exothermic liquid phase reaction by plotting them against the logarithm of the heating rate versus the reciprocal temperature. Hydroxymethyl formamide has been shown to be a major product of the liquid phase decomposition, which suggests that the decomposition of HMX in the liquid phase should be initiated by the N-N bond scission but not by the C-N bond scission.

1. Introduction

HMX, as the major ingredient of smokeless double-base propellants and as an energetic component of composite propellants, has recently occupied a key position in field of solid propellants. The kinetics and the mechanism of its thermal decomposition are of considerable importance, in as much as they relate to the stability of these materials and may also be involved in the combustion processes. An attempt has been made in this study to clarify the rate-determining steps in the weight loss process as a function of heating rate, to determine the kinetic parameters of each step and to obtain information as to a possible decomposition mechanism. A number of investigators have derived values for the parameters in the Arrhenius equation. The reported values of A (pre-exponential factor) and E_a (activation energy) are contained in Table 1. The agreement among the values as determined by the various experimental techniques is not very good. From Table 1, it seems to be probable that the decomposition mechanism varies depending upon the temperature range, although somewhat contradictory data on the temperature range are now available. A great deal of attention has been paid to the decomposition kinetics and mechanism of HMX below and above its melting point.

Until a recent revival of interest, the most comprehensive study of the thermal decomposition of HMX done by Robertson[1], who evaluated the kinetics above the melting point using the pressure-time curves of the evolved gases. Suryanarayana, Graybush and Autera[2] studied the thermal decomposition of nitro-^{15}N labeled HMX. Their results indicate that the thermal degradation of HMX proceeds by the predominant breakage of the C-N bonds but not by a breakage of N-N bonds and elimination of NO_2 groups.

The present paper describes a series of experiments designed to determine the variation of the rate-determining steps in the course of the decomposition by using thermoanalytical methods. Also, a new infrared spectroscopic approach was used to assign the nonvolatile products that correspond to each of the rate-determining steps in order to obtain some insight into the decomposition mechanism. The results obtained, thus far, indicate that four elementary processes appear in the HMX decomposition that depend on the heating rate. The liquid phase decomposition is almost certainly initiated by the breaking of the N-N bond and not by the breaking of the C-N bond.

2. Experimental

Apparatus and Procedure

This work was performed with a Shimadzu Model TGC-20 thermobalance[3], a Shimadzu Model DSC-20 differential scanning calorimeter and a Shimadzu Type 430 infrared spectrometer. The thermobalance has a sensitivity of 1 μg and capacities of heating a sample up to 900 °C in the open air, arbitrary gases and vacuum over the heating rate range of 0.5 °C/min to 40 °C/min. The use of simultaneous TG (thermogravimetry)-DTG (differential thermogravimetry) were conducted to determine an accurate thermogravimetry of HMX. The DSC (differential scanning calorimeter) apparatus used in this study is similar to the Perkin-Elmer Model DSC-1B in its structure and performance.

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Table 1. Kinetic Parameters for the Thermal Decomposition of HMX

Reported by	A[s^{-1}]	E[kcal/mol]	Reaction Order	Temperature Range [°C]	Method	Ref.
Robertson	$10^{19.7}$	52.7	1 (assumed)	271–314	Isothermal gas evolution method	1
Rogers and Morris	···	228 ± 24	···	Above M.P.	Dynamic DSC	11
Rogers and Smith	$10^{18.9}$	···	1 (assumed)	Above M.P.	Dynamic DSC	20
Maycock and	···	62	1 (assumed)	250–265	Isothermal TG	10
Pai Verneker		65	1 (assumed)	276–295	Dynamic DTA	
Suryanarayana and		45	1 (assumed)	226–245	Mass spec. study of decomp. products	21
Graybush	···	10–15	1 (assumed)	245–268		
		52	1 (assumed)	Above 268		
Hoondee	···	44.20	1 (assumed)	200–233		
		63.23	1 (assumed)	233–241	Dynamic DTA	22
		52.65	1 (assumed)	Above 241		
		65.79	1 (assumed)	232–241	Isothermal DTA	22
Rogers	6.4×10^{18}	51.3	0.7	270–285	Isothermal DSC	6
Rogers	1.51×10^{20}	52.9	0.6	273–285	Isothermal DSC	23
Takaira and Okazaki	···	146	1 (assumed)	280–300	Dynamic DSC	12
Goshgarian	···	29.9	1 (assumed)	200–240	Mass spec. study of decomp. products	16
		67.4	1 (assumed)	240–260		

All the TG-DTG and DSC measurements were conducted using an open-type aluminum sample cell (5.8 mm in diameter and 2.5 mm height). The complexity of the reaction was detected when a single perforated seal cell was used in the preliminary calorimetric measurements. It was found that no noticeable change appeared in the DSC traces in the temperature range before melting. Thus, the DSC was used exclusively in the kinetic study of the liquid phase decomposition and calorimetric studies.

The infrared spectroscopic measurements of the condensed products on a KBr plate were conducted under 1 atmosphere of pressure. The volatile products at the decomposition temperature were trapped directly on the KBr plate attached to the ceiling of the bell jar of the DSC as illustrated in Fig. 1. The temperature of the KBr plate might remain near room temperature during the test run. It was confirmed that no noticeable effects from the adhesive were found in the infrared spectra[6].

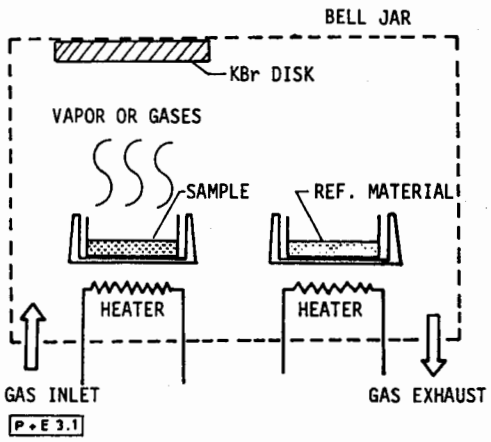

Figure 1. Schematic experimental setup for trapping the vapor and volatiles of the thermal decomposition of HMX using a DSC apparatus.

Materials

Fine HMX powder with an average particle diameter of 18 μm was used as received. It is produced by Chugoku-kayaku Co. Ltd., Hiroshima. This sample was sufficiently height enough in purity, since it showed the same melting temperature as that of HMX which had been recrystallized three times from acetone in the measurements with DSC.

Analysis

The Freeman Carroll method was used for the analysis of the TG-DTG data before melting occures[4]. It is desirable to analyze the thermoanalytical data by at least two different analytical methods in order to avoide an erroneous conclusion. Ozawa[5] states that the logarithm of the heating rate is in a linear relation with the reciprocal of the absolute temperature for the given conversion regardless of the reaction order. This method was also applied for reducing activation energies from the thermogravimetric curves of HMX below the melting point. In the preliminary experiments, the liquified HMX was found to decompose much more rapidly than the original solid phase decomposition. Thus, the DSC and TG-DTG data above the melting point were analyzed using the "peak temperature shift method" proposed by Ozawa.

3. Results

3.1. Decomposition kinetics studies

From a set of TG thermograms, the log (heating rate) versus the reciprocal of temperature for a given weight loss were plotted as shown in Fig. 2. It shows that two straight lines with different slopes exist depending upon the weight loss fraction. Activation energies calculated are: 38.0 kcal/mol in the weight loss fraction of 0.1–0.4, and 58.0 kcal/mol for that of 0.6. A smooth TG-DTG curve for about 2 mg of HMX measured with a heating rate of 0.5 °C/min was replotted on a plot of the

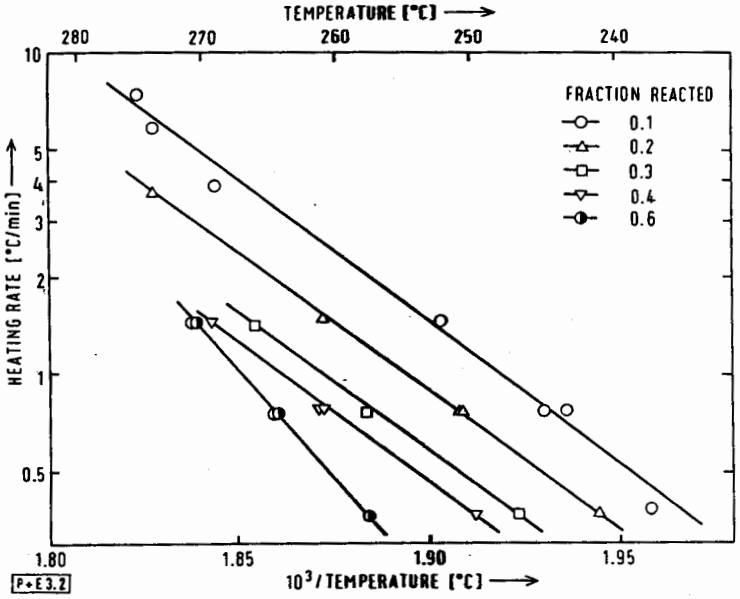

Figure 2. Effect of heating rate on the weight loss process of HMX below the melting point.

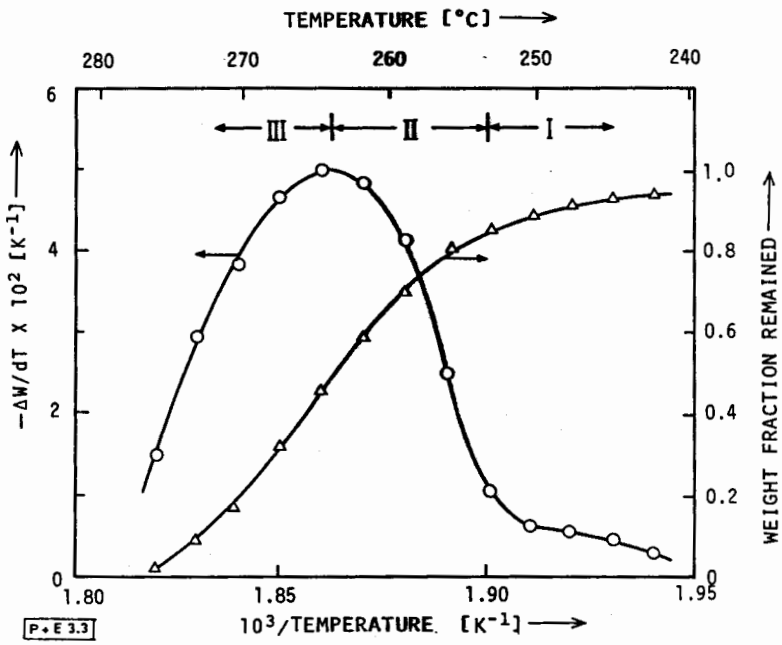

Figure 3. A typical TG-DTG curve of the solid phase thermal decomposition of HMX. The measurements were conducted using 2.08 mg of HMX (heating rate of 0.5 °C/min at 1 atm in the air).

reciprocal temperature versus the weight fraction remaining and the temperature derivative of weight loss, dW/dT, where W = sample weight, T = temperature as shown in Fig. 3. The Freeman and Carroll plot shown in Fig. 4 indicates that the weight loss process of HMX below the melting point includes three different processes. The apparent reaction order and the kinetics in each process are shown as follows:

Phase I, $\alpha < 0.2$, $n = -9$, $k = 1.2 \times 10^{24}\exp(-66{,}400/RT)$,

Phase II, $0.2 < \alpha < 0.55$, $n = 0$, $k = 2.5 \times 10^{7}\exp(-22{,}900/RT)$,

Phase III, $\alpha > 0.55$, $n = 1$, $k = 3.8 \times 10^{23}\exp(-61{,}800/RT)$,

where α = weight loss fraction, n = reaction order, k = reaction rate constant (1/s), R = universal gas constant, T = temperature.

Fig. 5 shows the effect of the heating rate on the peak temperature of DTG and DSC data above the melting point. The activation energies were determined to be 177 kcal/mol for the DTG measurements and 256 kcal/mol for the DSC data.

3.2. *Infrared spectroscopic studies on the nonvolatile products*

The results of the decomposition kinetic studies suggest that the course of the weight loss of HMX consists of several independent processes, and that one of the processes becomes the rate-determining step corresponding to the heating rate. Thus, it would be possible to detect the products produced in each process by selecting the heating rate and the upper limit of temperature properly. A new experimental approach based on this concept was actually performed with a combination of a sort of cold trap for IR measurements and DSC techniques (see Fig. 1). An infrared spectroscopic approach was choosen, since it enables one to obtain direct information about the molecular structure and to assign unknown high-boiling temperature products. Typical infrared spectra for various heating patterns are shown in Fig. 6 for the wave number interval of 800 cm^{-1} to 4000 cm^{-1}. All the measurements were conducted with a fixed ordinate expansion ratio of 5 in a flowing nitrogen

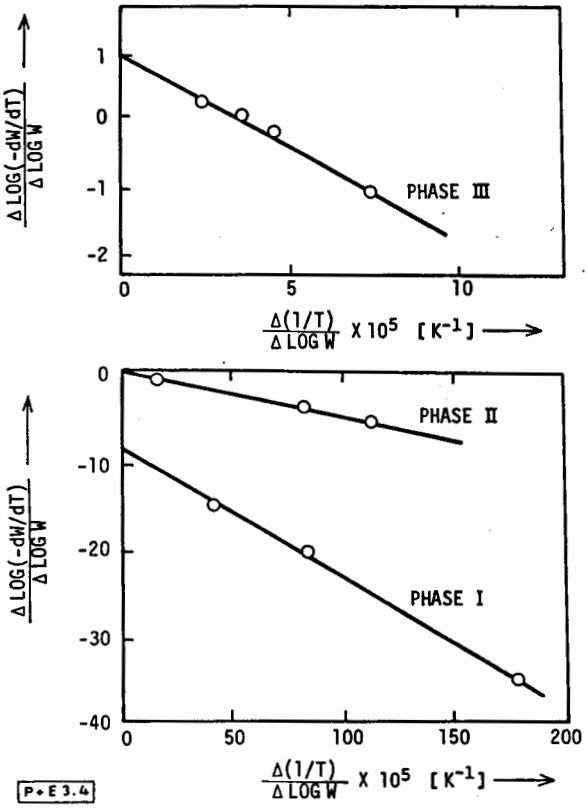

Figure 4. Freeman-Carroll plots of the TG-DTG data shown in Fig. 3.

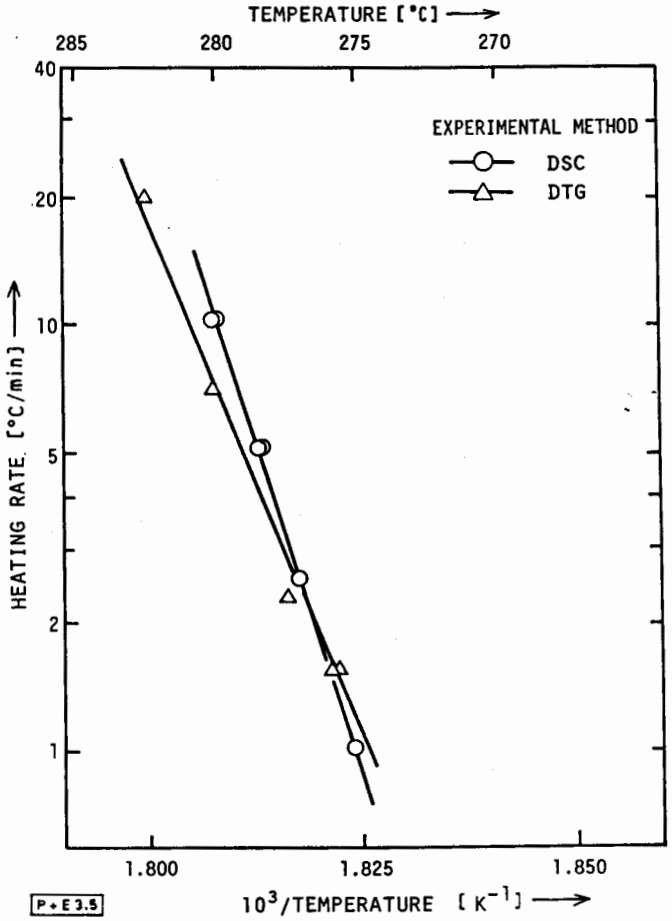

Figure 5. Effect of heating rate on the liquid phase thermal decomposition of HMX above the melting point. These were obtained by the peak temperature shift method of TG-DTG and DSC data.

atmosphere (40 ml/min). The spectrum of the products from a sample of about 1 mg HMX heated to 265 °C using a heating rate of 1 °C/min is identical to that of δ-HMX, which is formed due to the crystal phase change of β-HMX at 186 °C. A comparison of the infrared spectra between the upper and the

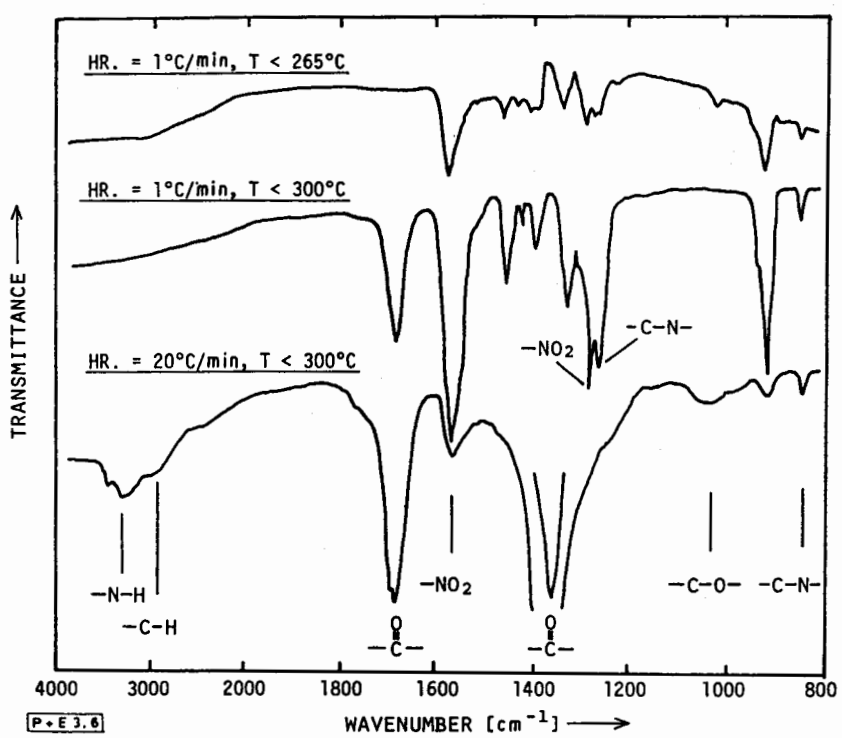

Figure 6. Infrared spectra of the nonvolatile products of HMX obtained under various heating conditions: The upper spectrum was identified as δ-HMX. In the middle one, the absorption peak at 1680 cm^{-1} was assigned to >C=O streching vibration in an amide compound as a solid phase decomposition. The lower spectrum was identified as hydroxymethyl formamide ($CH_2OH{\cdot}NH{\cdot}HCO$) that was found to be the major product of the liquid phase decomposition of HMX.

middle one shows that most of the absorption peaks in the spectra are the same. However, in a middle spectrum a new absorption peak is observed at 1680 cm^{-1}, which can be assigned to >C=O stretching vibration in an amide group. The appearance of this new absorption band suggests that some sort of decomposition reactions may occur in the temperature range from 265 °C to 285 °C at which the weight loss is completed.

A nonvolatile product evolved from the liquid phase decomposition was obtained by heating a sample of HMX up to 300 °C using a heating rate of 20 °C/min. It was noted that no noticeable weight loss was observed in the thermograms before the onset of its melting in this heating condition. The measured spectrum shown in the bottom in Fig. 6 identifies hydroxymethyl formamide as a major product.

4. Discussion

4.1. Effect of heating rate on sublimation and decomposition processes

The present work has revealed that the heating rate is a decisive parameter in determining what kind of elementary process appears and in what phase the decomposition occurs. The experimental results of the decomposition kinetic studies and the infrared spectroscopic studies are conclusively summarized in Fig. 7. The logarithm of the heating rate is plotted against the reciprocal of the absolute temperature for arbitrary weight losses. The detailed explanation of the scheme shown in Fig. 7 is described as follows: In the weight loss range less than 0.2, the Freeman-Carroll plot gives an apparent reaction order of –9. It is interesting to note that such a large negative order was reported by Rogers[6] in the initial phase of the decomposition of HMX with an isothermal DSC technique. As he pointed out, a relatively large negative order can be attributable to the early solid-state reaction during the induction time. This is easily understood from Fig. 3 where the initial part of the modified DTG curve shows the typical nature during the induction period.

It might be concluded that the induction period exists in the early stage of the weight loss process, however, the complete understanding of the observed negative order has not yet been accomplished. In the region where the weight loss ranges from about 0.2 to 0.5 below the melting point, sublimation is the rate determing step in the course of the weight loss process. The following experimental results support the fact that sublimation of δ-HMX is predominant in this region:

- a chemical kinetic feature of zeroth order reaction, relatively low activation energies, and low frequency factor indicate that sublimation is occuring
- the infrared spectrum of the product corresponding to the region discussed was assigned to δ-HMX.

A comparison between the obtained activation energy and a theoretically estimated one based on the measured heat of sublimation is shown as follows in order to confirm the presence of the sublimation process: Rosen and Dickinson[7] determined the heat of sublimation of β-HMX to be 41.89 kcal/mol. The heat of sublimation of δ-HMX may be approximated by subtracting the heat of transformation of β- to δ-HMX from the heat of sublimation[8] of β-HMX, thus the value would be 39.55 kcal/mol. According to Eyring[9], an activation energy of

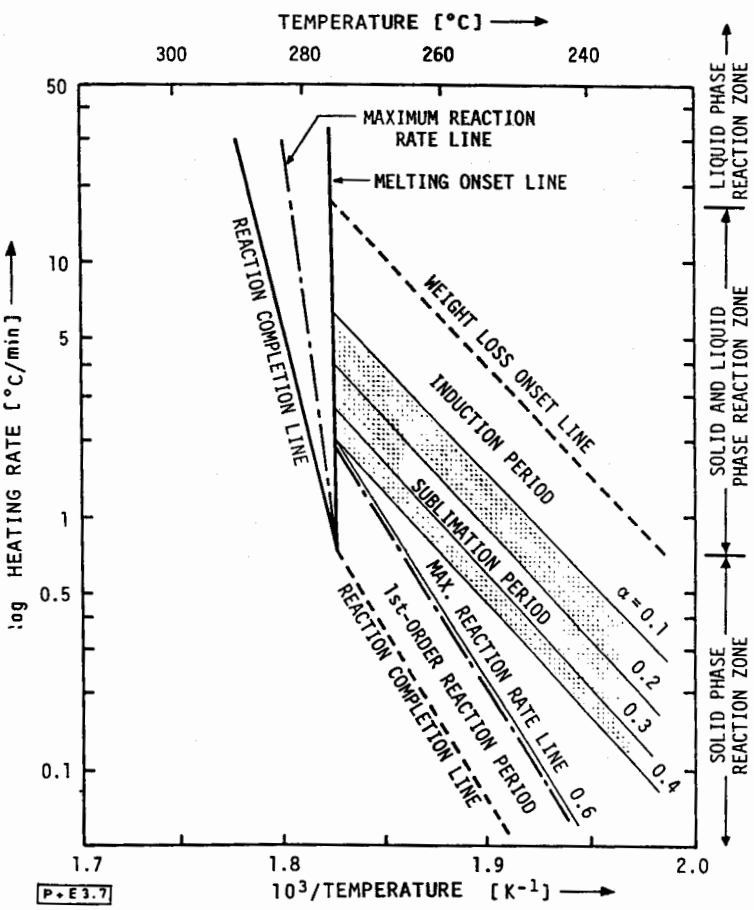

Figure 7. Reaction phase-change diagram of the thermal decomposition of HMX showing the decomposition process varies with heating rate.

sublimation can be obtained by subtracting RT from the heat of sublimation. Thus the activation energy of sublimation is estimated to be 39.45 kcal/mol. The measured activation energies in this investigation are 38.0 kcal/mol and 22.9 kcal/mol. The estimated value shows a close agreement with the observed one (38.0 kcal/mol).

The presence of the solid phase decomposition reaction has been confirmed and the activation energies were determined to be 58.0 kcal/mol and 66.4 kcal/mol. Maycock and Pai Verneker[10] reported the activation energy for the weight loss process in the temperature range of 250 °C to 265 °C to be 62 kcal/mol from a set of isothermal TG data. Only limited and somewhat contradictory data have been reported on the kinetics of the liquid phase decomposition of HMX. Rogers and Morris[11], and Takaira and Okazaki[12] determined the activation energies to be 228 ± 24 kcal/mol and 146 kcal/mol respectively, by using the dynamic DSC technique. These values are compatible to those obtained in this study, that is 177 kcal/mol (TG-DTG), and 256 kcal/mol (DSC). However, Robertson[1] determined an activation energy of 52.7 ± 2 kcal/mol with isothermal gas evolution measurements. Rogers[6] obtained an activation energy of 51.3 kcal/mol with the isothermal DSC technique.

No explanation has been offered for the large difference between the values of the activation energy for the liquid phase decomposition obtained by dynamic and static methods. Then a reasonable, though necessary tentative, interpretation for this problem has been offered in this investigation.

It is known that HMX has a heat of reaction of 200 cal/g to 250 cal/g in the liquid phase[12,13]. This was also recognized in this study, and thus a great deal of attention was taken to avoid a run-away-reaction by self heating. The occurrence of a run-away-reaction can be detected by the appearance of a shoulder on the temperature-time trace in the DSC thermogram. A sample weight of less than 1 mg, was used in this investigation. This was used to avoid the appearance of the shoulder in the heating rate range covered. It seems unlikely that a run-away-reaction would occur during the test run with a dynamic thermoanalytical technique under the experimental conditions used in this investigation.

Another possible explanation for the contradictory activation energy data might be given by the presence of an autocatalytic reaction. It would be conceivable from the analogy with RDX whose decomposition products are capable of reacting further with the residue in the condensed phase. The decomposition reaction of RDX, a closely related material to HMX, is known to be accelerated by its decomposition products, i.e., formaldehyde[14] and hydroxymethyl formamide[15]. Robertson[1] and Suryanarayana[2] et al. have reported that formaldehyde is one of the major products of the decomposition of HMX. Hydroxymethyl formamide has been found to be a major product in the liquid phase decomposition product in this investigation. Taking into consideration the similarity of the chemical properties and the reactivities between RDX and HMX, it seems likely that autocatalytic reactions may occur in the course of the liquid phase decomposition of HMX. Thus, the application of the peak temperature shift method may result in the reduction of erroneous kinetic parameters, since the method was derived on the assumption that one peak in a thermogram contains one chemical or physical process. Further experiments and discussion are necessary to clearly separate the primary and secondary reactions of HMX.

It is noted that the liquid phase reaction becomes dominant in the weight loss process of HMX with increasing heating rate as shown in Fig. 7. This also suggests that the liquid phase reaction becomes important in discussing the ignition and combustion processes of HMX. Boggs, Price and Zurn[13] have recently reported that the combustion of HMX at low pressures, below 500 psi, is characterized by gas evolution from/through the liquid covering the regressing surface. Fig. 7 indicates the appearance of a possible physical and chemical processes when HMX is subjected to heating at a constant rate, and also provides the theoretical basis for the proper heating rate to simulate this phenomenon of interest. In this sense, the plot of log (heating rate) versus 1/T shown in Fig. 7 can be called a "reaction phase-change diagram".

4.2. The mechanism of the liquid phase decomposition

It has been generally accepted that HMX decomposes in the condensed phase with the predominant breaking of the C-N bonds rather than the weaker N-N bonds. This is a hypothetical mechanism proposed by Suryanarayana[2] et al. from studies on isotopically labeled HMX. This hypothetical mechanism seems to be tacitly accepted as the decomposition mechanism for other nitramine compounds, i.e., RDX, in the condensed phase. Rauch and Fannelli[17] investigated the thermal decomposition mechanism of RDX above its melting point. They concluded that the decomposition occurs simultaneously in the gas phase and in the liquid phase, and further concluded that the decomposition mechanism for the gas phase is not the same as that for the liquid phase; the former almost certainly involves the breaking of the nitramino N-N bond and the formation of NO_2, whereas the latter does not. Batten[13] proposed a decomposition mechanism of RDX based on a study of the catalytic effects of its decomposition products and free radical traps on the rate of the thermal decomposition. According to the reaction scheme proposed by Batten, intermolecular bonding such as C . . . O and/or O . . . H is formed prior to the formation of nitrogen dioxide and formaldehyde as the primary products of the decomposition, and the secondary reactions involving nitrogen dioxide play an important role in the decomposition process.

Cosgrove and Owen[15] have studied the decomposition of RDX, and concluded that the major part of the reaction actually occurs in the gas phase and not in the solid. Nitrogen dioxide was not a product in any of these investigations, however, they found that hydroxymethyl formamide and its polymeric material are the major products, and that these materials act as both a solvent for RDX and a catalyst to enhance the reaction rate. Goshgarian[16] stated that the formation of HCN during the thermal decomposition of HMX is probably due to the N-N bond rupture in HMX together with ring rearrangement to form HCN. The thermal decomposition of solid HMX appears to occur through both C-N and N-N bond rupture, with the former being the more prevalent route.

To summarize these works, it seems most probable that the gas phase decomposition of nitramine compounds involves N-N bond ruptures. However, the condensed phase decomposition mechanism still obscure. This is attributable to the difficulties in separating the effect of the gas phase decomposition, and detecting the formation of nitrogen dioxide, since it readily reacts with the other products such as formaldehyde at the temperature range of interest. The infrared spectroscopic approach, used in this study, combined with the DSC technique has been shown to provide direct information on the decomposed products. It has been concluded that HMX produces predominantly hydroxymethyl formamide as a nonvolatile product in the process of homogeneous liquid phase

decomposition in this investigation. Because care must be taken to assure the absence of gaseous HMX, assignment of the nonvolatile product is not complicated by coexisting the reaction processes in different phases. The appearance of hydroxymethyl formamide as a product may suggest that HMX should decompose in a manner similar to the gas phase decomposition mechanism of RDX proposed by Cosgrove and Owen[15].

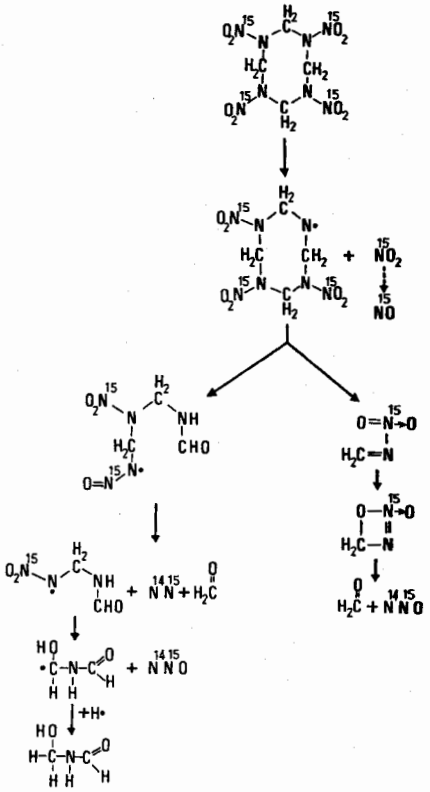

Figure. 8. A proposed mechanism on the liquid phase decomposition of HMX based on the experimental results obtained in this study.

A conceivable mechanism for the liquid phase decomposition of HMX is proposed in Fig. 8 on the basis of Consgrove and Owen. The difference in the number of the methylene nitramine group in a RDX and HMX molecule may result in the elimination of a mono-methylene nitramine molecule per one mole of HMX. The resulting mono-methylene nitramine possibly undergoes a simultaneous intermolecular oxygen transfer to the carbon and fissions of the C-N and O-N bonds, to give CH_2O and N_2O in accordance with the hypothetical mechanism proposed by Suryanarayana[2] et al. For the purpose of the detailed comparison of the observed decomposition products and according to Suryanarayana et al. with those predicted by the proposed scheme, the same ^{15}N-labelled HMX was assumed to be the starting material in Fig. 8. The nitrogen compounds expected from the proposed mechanism are N_2O, NO and N_2, and the mole ratio of their products is 2:1:1. Suryanarayana[2] et al. and Robertson[1] found the same nitrogen compounds as the major products and reported the obtained mole ratios to be about 4:1:1 and 1.5:1:1, respectively. Furthermore, exclusive appearance of isotopic species of $N^{14}N^{15}O$, $N^{15}O$ and $N^{14}N^{15}$ in the experiment can be completely explained according to the proposed hypothetical mechanism.

In conclusion, the predicted products based on the proposed decomposition mechanism are completely consistent with the measured ones obtained by other investigators both qualitatively and quantitatively. It should be noted that the formation of nitrogen dioxide can hardly be detected, since nitrogen dioxide reacts quite rapidly with formaldehyde, which has been recognized as a major product of HMX decomposition, over 200 °C. The overall reaction is represented[18] by

$$5\,CH_2O + 7\,NO_2 \rightarrow 3\,CO + 2\,CO_2 + 7\,NO + 5\,H_2$$

We have found no evidence in the course of these studies for any other gaseous products besides hydroxymethyl formamide.

Despite the lack of supporting chemical evidence, the production of hydroxymethyl formamide suggests that the first step in the liquid phase decomposition of HMX is the homolytic breaking of the nitramino N-N bond in a unimolecular process. It has been reported that the resonance of nitramino group stabilizes the N-N bonds. Although the considerably shorter N-N bond lengths, than the normal N-N single bonds, have been reported, the bond strength of the N-N bond does not seem to exceed that of the C-N bond. Since Llewellyn and Whitmore determined completely the crystal structure of ethylene dinitramine by X-ray crystallographic methods, and concluded[19] the N-N single bond separation being 1.40 Å and the double bond as 1.23 Å, then the observed bond distance of 1.33 Å is compatible with about the 15% double bond character. In other words, the N-N bond strength in ethylene dinitramine molecule is estimated to be about 53.4 kcal/mol. It is note to worthy that the estimated N-N bond strength is still less than that of the accepted C-N bond (≈70 kcal/mol). This indicates that the N-N bonds in a nitramine compound break easier than the C-N bond in the course of thermal decomposition in spite of the stabilizing effect due to the resonance of the nitramino group.

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