COMPARATIVE STUDIES ON THE DECOMPOSITION BEHAVIOUR OF SECONDARY EXPLOSIVES *RDX* AND *HMX*

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Thermal decomposition studies of *RDX* and *HMX* have been carried out by using Differential Scanning Calorimetric (DSC) technique where small amounts of the material could be used safely for analysis. The exothermicity for the thermal decomposition of *RDX* and *HMX*, in liquid state, was estimated to be 118 ± 12 Kcal Mole^{-1} and 140 ± 10 Kcal mole^{-1} respectively. The results very clearly indicate that under similar conditions *HMX* decomposes faster and releases more heat. The shape of the DSC thermogram of *RDX* and *HMX* both indicate that the decomposition follows a complex mechanistic path. Activation Energy (E) values were determined both from isothermal runs as well as dynamic runs and were found to be around 43±3 Kcal Mole^{-1} for both *RDX* and *HMX*. This suggests that the rate controlling process in the decomposition of both is same.

Nitramines are comparatively recent class of explosives and amongst them *RDX* and *HMX* are promising new candidates for small arms propellant formulations. In addition, they are also used as ancillary oxidisers in smokeless composite propellant compositions. Although a lot of work has been done on the thermal decomposition of these secondary explosives, the exact mechanism is by no means clear. It is surprising that the enthalpy data characterising decomposition, has hardly been used in the past to discuss the decomposition mechanism.

The purpose of the present work is to present a comparative study of the decomposition characteristics of *RDX* and *HMX* on the basis of Differential Scanning Calorimetric (DSC) data.

EXPERIMENTAL ASPECT

Differential Scanning Calorimeter (DSC-1B) and the accessories were obtained from Perkin-Elmer Ltd. The decomposition studies were carried out in a sealed aluminium pan with a hole at the top of the lid for the escape of gaseous products during the decomposition. *RDX* and *HMX* used were about 99% pure. *RDX* and *HMX* of definite particle size (35 to 76 microns) were used in all the experiments and the amount taken in each run was between 0·5 to 1·5 mg. Weighings were done on an electro-balance which was calibrated against a standard mass. Empty aluminium pan (identical in weight, shape and size) was used as a reference. Both sample and reference pans were covered with aluminium dome during the decomposition. The experiments were carried out in N_2 atmosphere. Dynamic measurements were made at scan speed of 4, 8, 16 and 32° K min^{-1} and range setting used were 4, 8, 16 and 32 millical sec^{-1} for full scale deflection on the recorder chart. Isothermal decompositions were carried out between 200° to 230° C for *RDX* and 250° to 265°C for *HMX*. The base-line under the scanning as well as isothermal thermograms were drawn as described in our recent publication[1]. Thermogram areas were measured with a planimeter which was checked against known area. Fraction decomposed (α) at a particular time was calculated by dividing the segmental area at that time by the total area. The enthalpy change under the endotherm/exotherm was calculated by comparing the area under the peak to that of the endotherm peak area of the standard Indium of known weight. Experimental conditions like chart speed, range, setting and scan speed were taken into account during the enthalpy evaluation.

RESULTS AND DISCUSSION

The phase-transition of β-*HMX* to the δ-form (Fig. 1) was found to occur in the temperature range of 184° to 194°C and the transition was found to be irreversible in agreement with earlier observations of Maycock and Pai Verneker[2]. The endothermic heat of phase-transition was also estimated. The data is presented in Table 1. *RDX* was observed to melt at 477·4 ± 0·2°K. The melting point was determined with respect to the melting point of tin obtained under identical scanning operation. Enthalpy data of *RDX* are also presented in Table 1. Average heat of fusion, obtained at various heating rates, was found to be 7·34 ± 0·6 Kcal mole^{-1} compared to the earlier reported value of 8·52 + 0·07 Kcal mole^{-1} by Hall[3].

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*Experimental data were obtained at the University of Leeds.

Table 1

Enthalpy data on *RDX* and *HMX*

Nature of Change	Enthalpy value (Kcal mole^{-1})	
	Experimental	Literature
HMX		
Phase transformation	2·1	2·25* 2·35±0·2†
Decomposition		
(*a*) Isothermal (251°—263°C)	133±6	—
(*b*) Scanning (4° to 32°C min^{-1})	140±10	166±9†
RDX		
Heat of fusion	7·34±0·06	8·52±0·07†
Decomposition		
(*a*) Isothermal (205°—230°C)	117·7	
(*b*) Scanning (2° to 32° min^{-1})	119·4	136±2†

* Ref. 8, † Ref. 3.

It was observed in *HMX* that after the phase-transition, a fusion endotherm is observed which is immediately followed by a sharp exotherm. The fusion-peak was observed at 284°C at the heating rate of 32°C min^{-1}. It was rather surprising to see that fusion endotherm could be obtained only at higher heating rates (16°K and 32°K min^{-1}) and not at the lower heating rates (8°K and 4°K min^{-1}). *HMX* exotherms at heating rates 4°C min^{-1} and 32°C min^{-1} are shown in Fig. 1. Maycock and Pai Verneker[2] have also observed in their DTA studies that the fusion endotherm is obtained only at heating rates above 8°C min^{-1} and not below it. No explanation for this behaviour, however, is available. The most plausible explanation for this may be that the percentage decomposition at any temperature during slow decomposition may be more compared to the corresponding value at a faster heating rate. Since *HMX* is known to decompose prior to melting, the heat of decomposition in low scan rate is sufficient enough to melt the sample and thus endothermic peak does not appear. The attribution of the absence of a fusion endotherm to heat supplied by the decomposition seems to be quite sound since a number of cases exist in which a process with a large $\triangle$H masks a process with the opposite sign and low $\triangle$H. It is thus, safe to assume that decomposition proceeds both with and without melting. In *RDX* the melting endotherm was observed at all the heating rates. It may be mentioned here that although both *RDX* and *HMX* melt before the extensive decompositions the gap between the melting endotherm and the subsequent exotherm is larger in *RDX* compared to *HMX*.

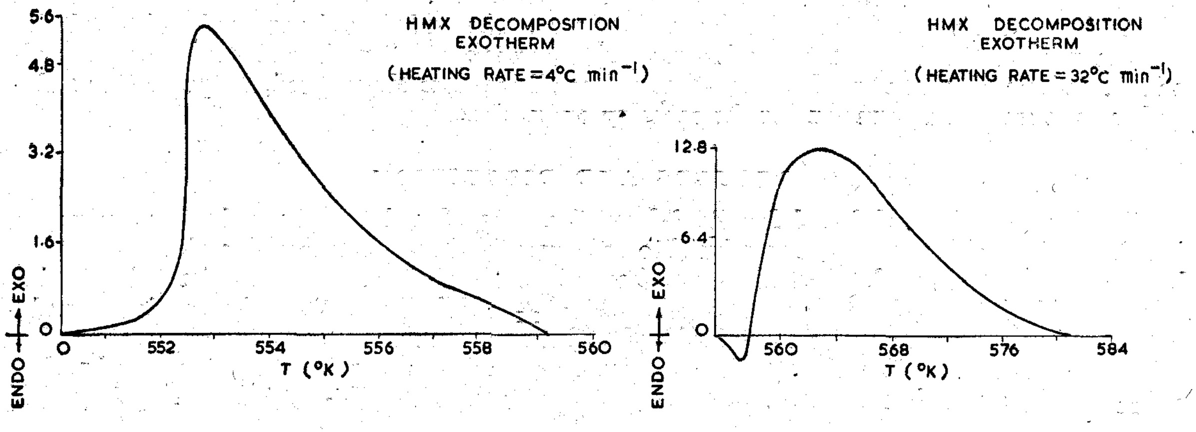

Fig. 1—Typical DSC thermogram of *HMX* in scanning mode of decomposition.

The general pattern of the kinetic behaviour can often be obtained by visual inspection of the decomposition curves. The isothermal as well scanning exotherms of both *RDX* and *HMX* (Fig. 2) do not show a symmetrical smooth single peak suggesting that they do not follow a single one-step decomposition process. Various kinetic equations for solid state decomposition have been tested and the tests show that none of the standard first order, second order, power equation or autocatalytic equations gives a good fit for the entire range of decomposition. From this observation, and from the nature of decomposition as shown in Fig. 2, it could be concluded that both *RDX* and *HMX* follow complex decomposition process. Analysis of the DSC curves have been made to calculate the activation energy (E) with a general procedure equally applicable to scanning and isothermal runs. The procedure gives E data which is free from any kinetic assumptions or topochemical model. It need not be mentioned here that sometimes wrong kinetic assumptions lead to erroneous E values. The E calculations in the scanning mode do not refer to a single scanning run but to a combination of various scanning runs. Before attempting to calculate E the thermograms obtained both in isothermal and scanning operations were reduced to α (fraction decomposed) versus time plots as shown in Fig. 3 and 4 both for *RDX* and *HMX*. The details of the procedure for E calculation are given below :—

If $\triangle H$ is total exothermicity (cal gm^{-1}) under the curve and dm/dt (gm sec^{-1}) is the rate of decomposition (i.e., weight loss rate) then the ordinate deflection Z (millical sec^{-1}) can be written as

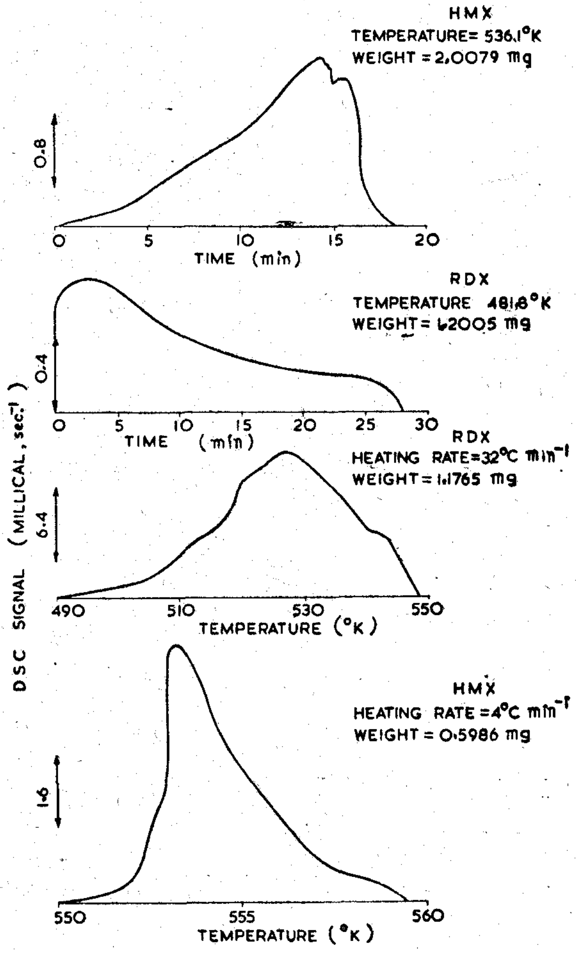

Fig. 2—Typical DSC thermograms of *RDX* and *HMX* in scanning and isothermal operations.

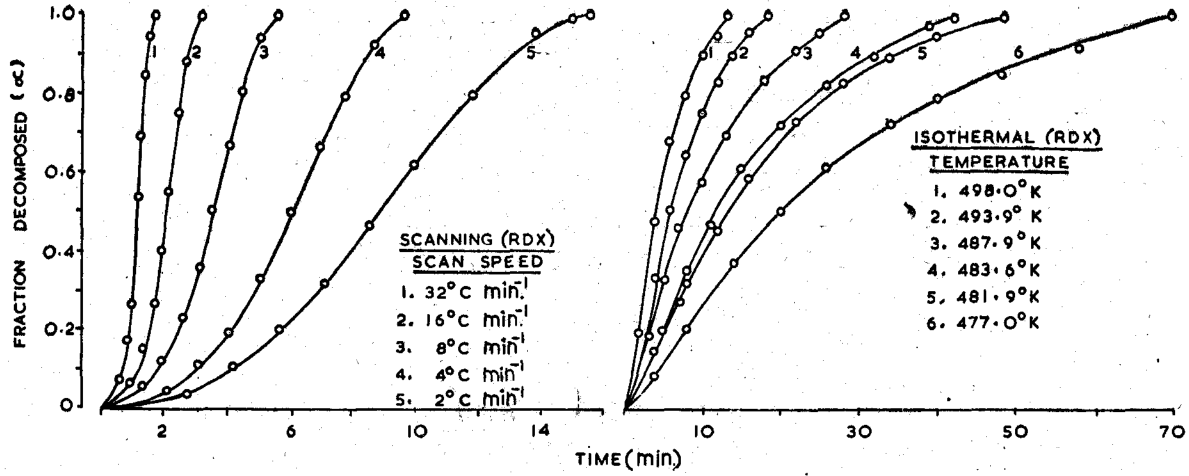

Fig. 3—Fraction decomposed (α) versus time plot for *RDX* decomposition in scanning and isothermal operation.

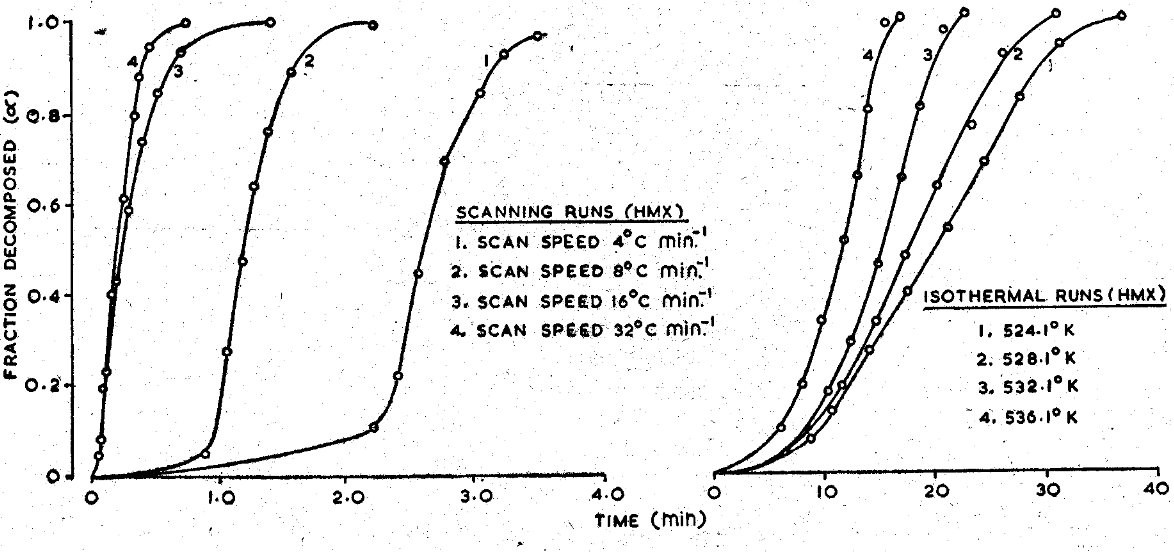

Fig. 4—Fraction decomposed (α) versus time plot for *HMX* decompositions in scanning and isothermal operation.

$$Z = \frac{dm}{dt} \triangle H$$

$$\text{or} \qquad \frac{dm}{dt} = \frac{Z}{\triangle H} \tag{1}$$

We have assumed that the kinetics of decomposition can be expressed as separable function of the extent of decomposition and temperature as follows :—

$$\frac{d\alpha}{dt} = f(\alpha)\, k(T) \tag{2}$$

Equation (2) can be written in a general form as follows

$$\frac{d\alpha}{dt} = k(1-\alpha)^n, \; n = \text{order of reaction} \tag{3}$$

It is evident that the temperature dependence can be expressed by an Arrhenius type relationship as follows.

$$K = A \exp\left(-\frac{E}{RT}\right) \tag{4}$$

Where E is the activation energy for decomposition in cal mole^{-1}

On combining equations (1), (3) and (4) we get

$$\frac{d\alpha}{dt} = \frac{dm}{dt} = \frac{Z}{\triangle H} = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{5}$$

If α and n are maintained constant in equation (5) then

$$\frac{Z}{\triangle H} = B \exp\left(-\frac{E}{RT}\right) \tag{6}$$

where

$$B = A(1-\alpha)^n$$

Equation (6) is equally valid for both scanning as well as isothermal thermograms provided the necessary conditions are satisfied. The plot of $\log Z/\triangle H$ versus $1/T$ will directly yield the value of E. The essential condition in the validity of this procedure, as pointed out above, lies in the fact that α and n should be maintained constant for different scanning operations. α versus time or α versus temperature plots can be used to determine the temperature at various heating rates for any fixed value of α. The condition that n should be constant required the kinetic behaviour at different heating rates (different temperatures in isothermal runs) should be same. This is verified from the so called reduced-time plots where α versus time plots at various heating rates (or temperatures) are superimposed on each other. Mathematical justification of such a reduced-time plot has recently been worked out[4]. Reduced-time plots in a dynamic as well as isothermal runs for both *RDX* and *HMX* are shown in Fig. 5, 6 and 7. The plots very clearly reveal that the E estimations can be carried out without any difficulty for *RDX* and *HMX* isothermal runs and for *RDX* in scanning runs. The E data are given in Table 2. It may be noted that E values obtained both from scanning as well isothermal operations agree with each other for *RDX*. This gives credence to the method used for E estimations.

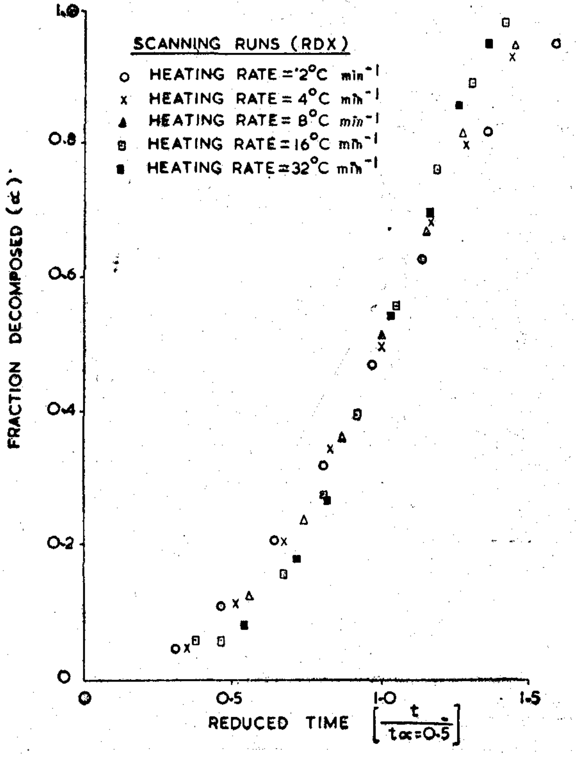

Fig. 5—Fraction decomposed (α) versus reduced-time plot for *RDX* decomposition in scanning mode.

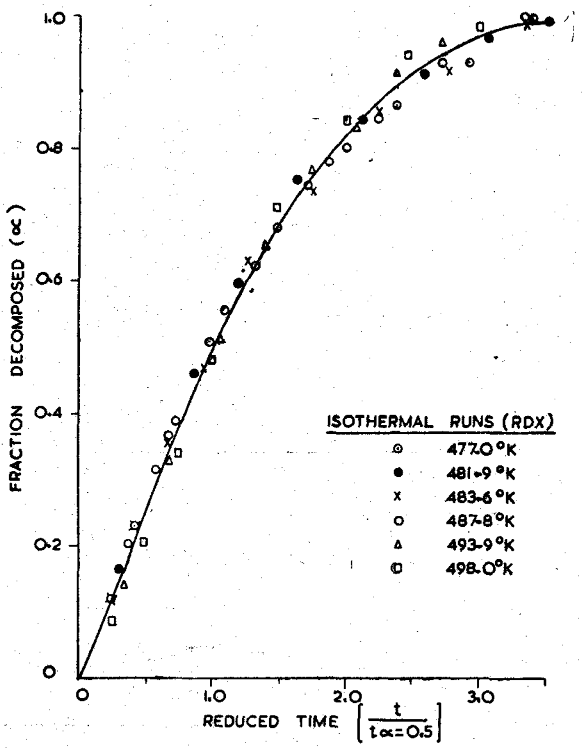

Fig. 6—Fraction decomposed (α) versus reduced-time plot for *RDX* decomposition in isothermal mode.

Reduced-time plots of *HMX* show similarity for scanning runs at 4° and 8°C min^{-1} in one set while for 16° and 32°C min^{-1} in another set. This can be explained on the basis of the partial melting observed in the later case. From the result we also see a significant error in the E estimations (Table 2) for scanning runs. This observation leads to the following problem. The occurrence of some melting diminishes the evolution of heat and therefore yields a lesser calculated value of α. Any dynamic run or higher temperature isothermal runs will have an error which is neither avoidable nor measurable. The consequence of this is that the kinetic parameter calculated from dynamic measurements are not reliable nor are those from isothermal runs above the melting point. A good reduced-time plot obtained in the present work in isothermal operations may be due to the fact that a narrow temperature range has been selected *i.e.* 252° to 264°C.

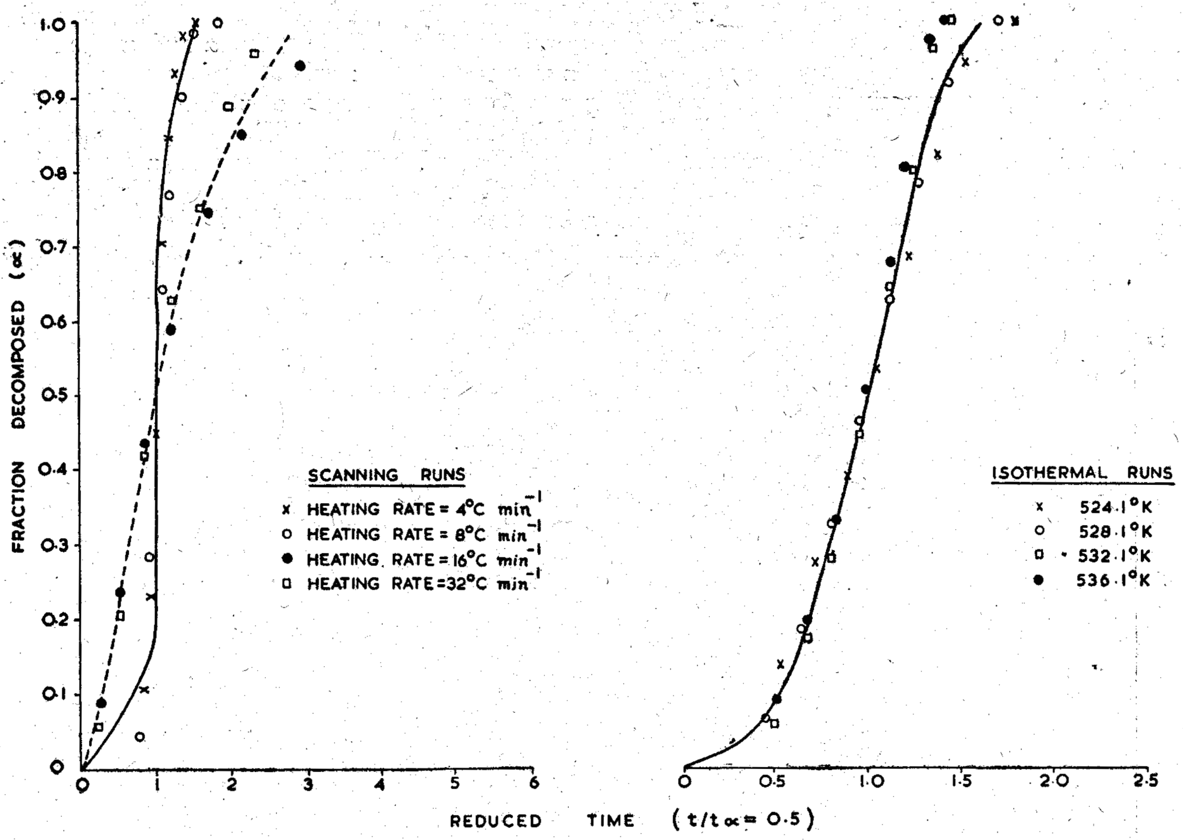

Fig. 7—Fraction decomposed (∝) versus reduced-time plot for *HMX* decomposition in scanning and isothermal mode.

TABLE 2

E DATA OF *RDX* AND *HMX* DECOMPOSITION (EXPERIMENTAL)

Experimental conditions	E(Kcal mole^{-1})	Method of Eestimation (References)
HMX		
Isothermal (251°—264°C)	42±2	9
Isothermal (252°—263°C)	44±2	10
Scanning (4° to 32°C min^{-1})	46±10	9
RDX		
Isothermal (207° to 227°C)	41±1	9
Isothermal (207° to 227°C)	38±1	10
Scanning (2°—32°C min^{-1})	42	11
Scanning (2°—32°C min^{-1})	42±3	9

Various other reported E values from literature are given in Table 3. Higher values reported by Rogers and Morris[5] and Hall[3] for *HMX* should not be taken with seriousness because the method involved for E calculation has no available kinetic justification. Values of E for *RDX* and *HMX* decomposition reported by previous workers (Table 3) generally lie within the error limit established in the present investigation. Table 2 further reveals that E for both *RDX* and *HMX* are similar in magnitude which is not surprising

TABLE 3

E DATA OF *RDX* AND *HMX* DECOMPOSITION (LITERATURE VALUES)

(Kcal mole^{-1}) E	Temperature Range (°C)	Reference
RDX		
47·5	213—299	12
67·5	(Scanning)	5
45·5	203·5—261	13
67·0	179—200	14
45·2	210—216	3
HMX		
52·7	271—314	12
228±2	Scanning	5
50·3±6·4	Scanning (*HMX* taken in convalex 10 solvents)	5
51·3	271—285°	15
180—210	Scanning	3
65	Scanning	2
59—62	245—280°C	2
44·2	220°—233°C	13
63·2	233°C—241°C	13
52·6	241°C	13

since both compounds have a ring structure of same basic unit of $-CH_2N\ (NO_2)-$. In both compounds rapid decomposition takes place in liquid-phase since the liquid-phase gives suitable environment for the decomposition of the material. It may be mentioned here that Suryanarayana *et. al*[6] have suggested on the basis of ^{15}N tracer study of the *HMX* decomposition products that there is a strong evidence for the cleavage of the *N-C* bond during the decomposition. The same mechanism may also hold in the *RDX* as well.

Fig. 8 and 9 present the results, of the time taken for complete decomposition and maximum reaction rate of *RDX* and *HMX* at various heating rates. Both of these parameters are higher for *HMX* compared to *RDX*. Table 1 on the other hand presents the data on the heat of decomposition of *RDX* and *HMX* where it may be seen that the heat of decomposition of *HMX* is higher compared to *RDX*. Thus, the results presented in Fig. 8 and 9 and Table 1 very clearly indicates that *HMX* decomposes faster than *RDX*. This may have a bearing on the fact that *HMX* possesses a higher detonation velocity than RDX[7].

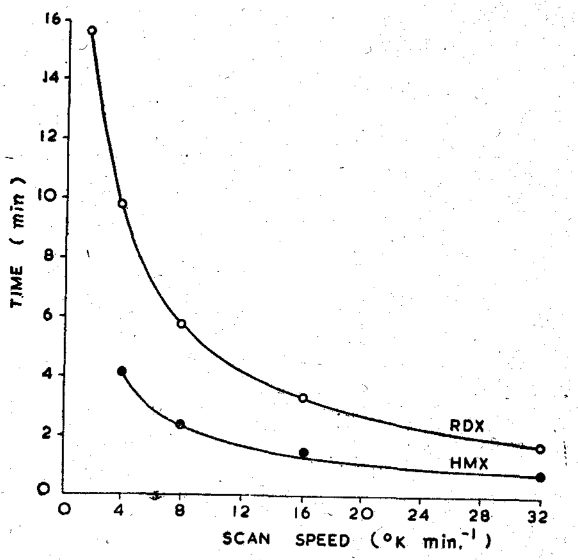

Fig. 8—Comparison of the time for completion of decomposition in *RDX* and *HMX* at various heating rates.

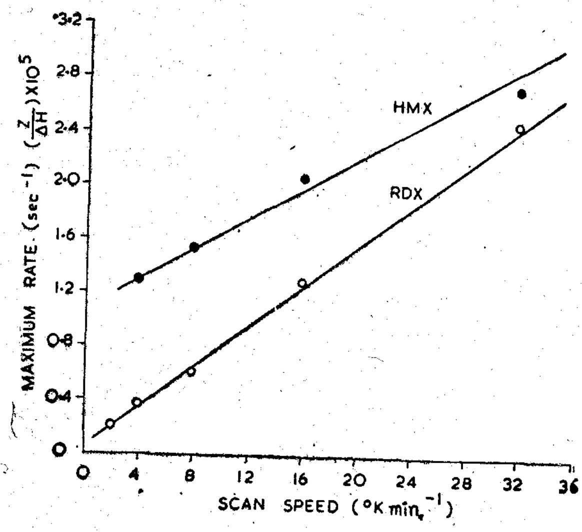

Fig. 9—Comparison of the maximum reaction rate for *RDX* and *HMX* decomposition at various heating rates.

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