Thermochimica Acta, 7 (1973) 57–67
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MELTING AND DECOMPOSITION OF RDX–HMX MIXTURES BY DTA

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(Received 5 March 1973)

ABSTRACT

The melting and decomposition behavior of various RDX–HMX mixtures was studied by DTA (the HMX apparently existed in the δ-polymorphic form during the physical and chemical changes which occurred). Non-cyclic heating programs (thermodynamically unstable states existed) and cyclic heating and cooling programs (H/C/H) (thermodynamically stable states existed) were employed. Data from those programs indicated that solid solutions of RDX–HMX occurred in the composition range of *ca.* 55–83 wt % RDX. Thus, below this lower limit, HMX separated from the mixture while above the upper limit, RDX separated. From the van't Hoff freezing point relation for eutectic equilibria, the heat of fusion of RDX (ΔH_A^f) was estimated as *ca.* 33 cal g^{-1}.

When a cyclic run was carried out for a mixture containing less than 55 wt % RDX, a single endotherm resulted (presumably, melting of a 55 wt % solid solution) followed by two strong exotherms. The first exotherm was attributed to decomposition of the 55 wt % solid solution while the second to HMX decomposition. Upon subjecting an RDX–HMX mixture containing more than 83 wt % RDX to a H/C/H program, two endotherms appeared followed by a single strong exotherm. The endotherms were ascribed to melting of an 83 wt % solid solution and of RDX, respectively. The strong exotherm was attributed to concurrent decomposition of RDX and the 83 wt % solid solution (no HMX exotherm could be detected). When mixtures containing *ca.* 55–83 wt % RDX underwent cyclical programs, only one endotherm and only one exotherm could be observed. The endotherm resulted presumably from melting of a solid solution whereas, the exotherm from decomposition of the solid solution.

From the data obtained, approximate phase diagrams were constructed for the melting and decomposition of RDX–HMX mixtures based upon cyclic and non-cyclic programs.

INTRODUCTION

In the course of investigating compatibility of highly energetic materials, *e.g.*, RDX and HMX, with various polymers by DTA, the decomposition activation energy (E) of an admixture of RDX and HMX was estimated[1]. It was found that the value of E of neat RDX dropped from 80 to 66 kcal mole^{-1} upon admixing RDX with HMX (82 wt % RDX; *cf.* runs RDX-1, 1B, and 13 in ref. 1). Subsequently, other mixtures of RDX and HMX in varying proportions were studied by DTA. DTA has been utilized in the past to determine phase diagrams of various mixtures[2,3].

The purpose of this paper is to report on the melting and decomposition behavior of various RDX–HMX mixtures by DTA. To the best of the author's knowledge, there is relatively little information available on this subject in the literature[4]. Further work would be desirable in this area utilizing X-ray and hot stage microscopy techniques. For this reason, this report should not be considered as final.

EXPERIMENTAL

Starting materials

Cyclotrimethylene trinitramine (RDX) was recrystallized from acetone and γ-butyrolactone, m.p. (onset) = 203 °C (the RDX used was obtained through the courtesy of J. R. Autera); cyclotetramethylene tetranitramine (HMX), β-polymorph, was extracted with ethylene dichloride and recrystallized several times from acetone (courtesy of J. R. Autera).

Other materials used were: tin, indium, and zinc standards (duPont, DTA grade, for calibration purposes), and aluminum oxide.

Apparatus

A duPont 900 Differential Thermal Analyzer was employed with a heating block which accommodated 4 mm capillaries.

Procedure

From 0.1 to 4.1 mg RDX were mixed with from 0.2 to 5.0 mg HMX, and 17 to 22 mg alumina were placed above the admixture (mixture compositions varied from 9 to 95 wt % RDX). A Chromel–Alumel thermocouple tip was inserted into the admixtures and *ca.* 19 mg alumina was used as the reference material. The atmosphere surrounding the sample was still air, a heating rate of 6 °C/min was employed throughout, and admixing was accomplished using a fine metal wire. Thermograms were also obtained on neat RDX and neat HMX.

Besides heating programs, RDX–HMX mixtures (and the neat materials) were subjected to heating, cooling, and reheating cycles (H/C/H). Thus, generally, an admixture was heated to *ca.* 200–202 °C and maintained at this temperature range for *ca.* 10 min. The mixture was then air-cooled at a rate of *ca.* 4–5 °C/min, to *ca.* 110 °C and the mixture subsequently reheated to complete decomposition.

Thermocouple temperatures were calibrated in the temperature range of interest by using tin and indium standards. Further, these standards (along with zinc and benzoic acid) were employed to calibrate thermogram areas in terms of caloric units in order to obtain semi-quantitative estimates of thermal heats of decomposition (ΔH_{dec}) and heats of fusion (ΔH_f).

It may be apropos here to note that trace amounts of impurities in such highly energetic materials as RDX and HMX *may* have pronounced effects on their decomposition behavior[1]. Further, physical changes may be dependent upon rate of heating[5] (heating rate, therefore, was maintained constant throughout this study).

RESULTS AND DISCUSSION

As previously indicated, neat RDX commences to melt at *ca.* 203 C and the melting is apparently over at *ca.* 210 C (*cf.* Table 1). Soon thereafter a strong exothermic peak commences denoting RDX decomposition. This exotherm is over at *ca.* 245 C. (As previously indicated, still air and a heating rate of 6 C/min were employed throughout the DTA runs). In the case of neat HMX, a small endotherm commences to appear at *ca.* 190 °C and is over at *ca.* 194 C. Thereafter, at *ca.* 281 °C, a strong exotherm occurs, signifying HMX decomposition. Under the experimental

TABLE 1

MELTING OF NEAT RDX BY DTA

RDX Run. no.	*Heating program*	*Initial endotherm melting range (no cycle run) (C)*	*Final endotherm melting range (cyclic run) (C)*
1A	heat	203–210	
1C	heat	203–209	
1D	heat	203–209	
1G	heat	203–209	
1H	H/C/H[a]		203–210

[a] Heated to *ca.* 200 C and maintained at this temperature *ca.* 10 min, then air-cooled to *ca.* 110 C, and finally reheated to complete decomposition.

TABLE 2

TRANSITION AND DECOMPOSITION TEMPERATURES OF NEAT β-HMX BY DTA

HMX run no.	*Heating program*	*Initial transition temperature (C)*	*Initial decomposition temperature (°C)*
1A	heat	188	
1B	heat	189	281
2A	heat	189	280
2B	heat	189	281
2C	H/C/H[a]	190[b]	280

[a] Heated to *ca.* 200 C and maintained at this temperature *ca.* 10 min, air-cooled to *ca.* 130 C, and reheated to decomposition. [b] Upon reheating sample after annealing, the transition endotherm could no longer be detected.

conditions used, this exotherm is over at *ca.* 288 °C. The small endotherm beginning at 190 °C is reportedly a transition from the β- to the δ-polymorph of HMX (*cf.* Table 2). Thus, the δ-HMX is the polymorphic form which is essentially involved in this investigation. In this connection, it may be remarked that the various polymorphs of HMX possess different physical and chemical properties[6] so that the melting and decomposition behavior of RDX–HMX mixtures undoubtedly depends upon the HMX form present in contact with the RDX during the physical and chemical changes which occur.

For all mixtures of RDX–HMX investigated, using a heating program only, a relatively large endotherm was obtained which commenced at *ca.* 188–189 °C. That this initial endotherm was a result of the polymorphic transition of HMX was obviated in the following manner. Neat HMX was heated to a temperature beyond its transition endotherm and the temperature was maintained (200–202 °C) for *ca.* 7 min after which the sample was air-cooled to *ca.* 130 °C and then reheated to decomposition. Upon reheating, no transition endotherm could be detected (the δ-form is apparently very stable under the conditions employed). Another run was then carried out in which neat HMX was again maintained at a temperature beyond its transition endotherm; however, after cooling to *ca.* 120 °C, RDX was added to the HMX (due to convenience of sample manipulation, this particular run was carried out using DSC). Upon reheating, an endotherm commenced at *ca.* 190 °C (this endotherm of the mixture was markedly pronounced as compared with that for the neat HMX). These and other results (which will be given subsequently) suggested that when mixtures of RDX and HMX were heated, a metastable solid solution resulted which commenced melting at *ca.* 190 °C. That this latter temperature resulted from a metastable condition could be demonstrated as follows. Various mixtures of RDX and HMX were prepared and subjected to a H/C/H cyclic program. Depending upon composition, various endotherms were obtained whose initial melting temperatures varied from *ca.* 166 to 185 °C and whose final melting temperatures varied from *ca.* 174 to *ca.* 199 °C. These cyclic runs indicated that below *ca.* 55 wt % RDX, the final melting temperatures did not drop below *ca.* 174 °C. Thus, it appeared that a solid solution of 55 wt % RDX composition resulted as more and more HMX was added to RDX. When more than 45 wt % HMX was added, a saturated solid solution resulted and excess HMX separated out. Upon subjecting such a mixture to a H/C/H cycle, a final melting point of *ca.* 175 °C was attained followed by a strong exotherm (presumably, decomposition of the 55 wt % solid solution) and another final exotherm corresponding to HMX decomposition (*cf.* Fig. 1A). In a similar manner, cyclic runs were employed to ascertain that above *ca.* 83 wt % RDX, the final melting temperatures did not exceed *ca.* 199 °C (*cf.* Table 3, RDX-38). Thus, it appeared that a solid solution of *ca.* 80 wt % RDX formed as more and more RDX was added to HMX. When more than 83 wt % was added a saturated solid solution resulted and excess RDX separated out. Upon subjecting such a mixture to a H/C/H cycle, a final melting point of *ca.* 197–199 °C was attained followed by an endotherm commencing at *ca.* 202 °C (presumably the melting of the excess RDX) and ending at 209 °C which in turn was followed by a

TABLE 3

MELTING AND DECOMPOSITION OF VARIOUS RDX-HMX MIXTURES IN STILL AIR

RDX		*Heating program*	*RDX Out?*	*HMX Out?*	*Initial endotherm melting range (no cycle run) (°C)*	*Final melting point (cyclic run) (°C)*
Run no.	*Wt %*					
13	82	heat	sl.	no	188–196	
14	55	heat	sl.	yes	188–196	
15	89	heat	yes	no	189–196	
16	52	heat	yes	yes	188–196	
17	32	heat	yes	yes	188–195	
18	52	H/C/H[a]	no	yes	189	175
19	58	heat	no	sl.	189–196	
20	85	H/C/H	no	no	190	197
21	83	H/C/H/C/H	sl.	sl.	189	195
22	48	H/C/H	no	yes	190	174
23	70	heat	no	no	189–197	
24	70.5	H/C/H	no	no	189	188
26	69	heat	no	no	190–197	
27	58	heat	sl.	sl.	190–196	
28	80.5	H/C/H	sl.	no	190	195
29	71.5	H/C/H	no	no	189	190
30	62.5	heat	no	sl.	189–196	
31C	66.5	H/C/H	no	no	189	187
31C′	63	H/C/H/C/H	no	sl.	189	185
32	22	heat	yes	yes	189–195	
35	88	H/C/H	yes	no	189	197
36	25	H/C/H	no	yes	189	174
38	95.5	H/C/H	yes	no	190	199
39	9	H/C/H	no	yes	189	175

[a] See Experimental.

strong exotherm which began almost immediately after the end of the endotherm. This exotherm was over at *ca.* 250°C and is presumably due to the concurrent decomposition of RDX and an 83 wt % solid solution of RDX–HMX. No HMX exotherm could be detected up to a temperature of *ca.* 295°C (*cf.* Fig. 1B).

From the preceding, it would appear that between RDX compositions of *ca.* 55–83 wt % solid solutions should result. To check this, various heating cycles were carried out in which such compositions were employed. These runs as well as various others are listed in Table 3. From this table it can be seen that for 70.5 wt % RDX (*cf.* RDX-24, a cyclic run), a melting endotherm with a final melting temperature of 188°C was attained. Thereafter, no RDX melting endotherm was observed; a strong exotherm commenced at *ca.* 202°C and was over at *ca.* 249°C. This strong exotherm apparently involved the decomposition of a solid solution consisting of 70.5 wt % RDX; no HMX exotherm could be observed (*cf.* Fig. 2A). Since no RDX melting endotherm or HMX decomposition exotherm was observed in

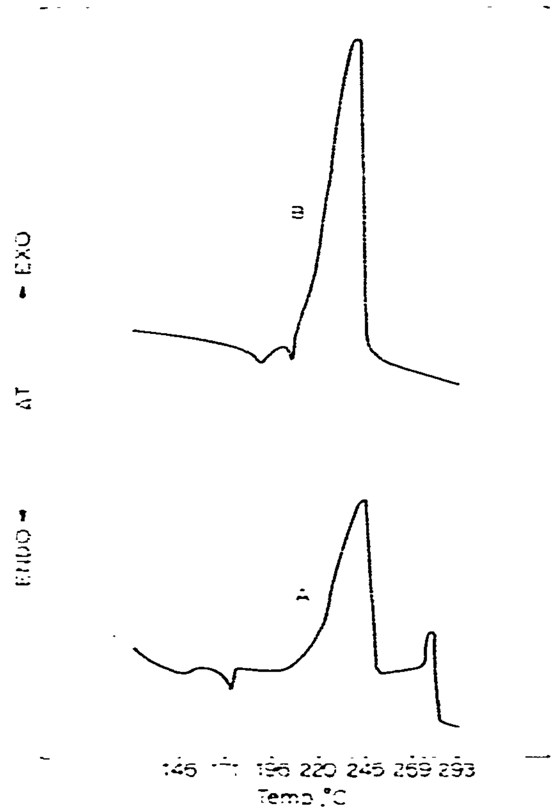

Fig. 1. (A) DTA trace of final heating stage of cyclical run RDX-18; (B) DTA trace of final heating stage of cyclical run RDX-35.

RDX-24. Table 3 indicates that no RDX or HMX separated out of the solid solution for this run. In this connection, it can be seen from Table 3 that no RDX or HMX separated out during cyclic runs when RDX compositions of 80.5 wt % (*cf.* RDX-28) or 63 wt % (*cf.* RDX-31C′) also were employed. Thus, it is apparent that solid solutions of RDX–HMX result in the RDX composition range of *ca.* 55–83 wt %.

Besides cyclic runs, various non-cyclic programs were carried out which tend to corroborate the results obtained for the cyclic runs. Thus, when an RDX composition of 70 wt % was used (*cf.* RDX-23, Table 3) in a heating only programmed run, no RDX or HMX separated out. Similar results were obtained for RDX compositions of 58 (*cf.* RDX-19, 27), 62.5 (*cf.* RDX-30), and 82 wt % (*cf.* RDX-13). In these non-cyclic runs, the melting point range varied from *ca.* 188–197 °C, indicating that initially a metastable solid solution of *ca.* 83 wt % RDX formed. Presumably after the melting phase, a more thermodynamically stable solid solution formed so that in the RDX composition range of *ca.* 55–83 wt %, no RDX or HMX separated out on subsequent heating (*cf.* Fig. 2B and Table 3). However, for RDX compositions outside of this range, it was observed that RDX and/or HMX separated out for both cyclic and

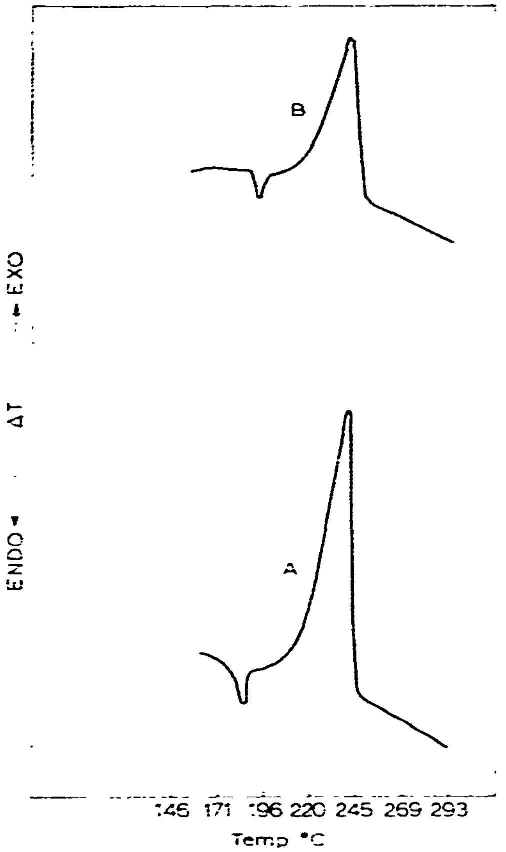

Fig. 2. (A) DTA trace of final heating stage of cyclical run RDX-24; (B) DTA trace of heating only run RDX-23.

non-cyclic runs. Thus, for the non-cyclic programmed runs, when the percentage of RDX varied from 22 to 52 (*cf.* RDX-16, 17, 32) both RDX and HMX separated. This may be ascribed to the formation of thermodynamically unstable solid solutions. Thus, whereas in RDX-32, a non-cyclic run, an RDX composition of 22 wt % resulted in the separation of both RDX and HMX, a cyclic run (RDX-36) in which 25 wt % RDX was used afforded only the separation of HMX, as anticipated. Similar results can be observed from a comparison of runs RDX-16 and 18 wherein 52 wt % RDX was employed. When the RDX composition was considerably above *ca.* 83 wt % (*cf.* RDX-15, 35, 38), only RDX separated out for either a cyclic or non-cyclic run, as anticipated (due to experimental limitations, the RDX content in mixtures was restricted to 9–95 wt %).

Based upon the preceding, it can be seen that at RDX contents of *ca.* 55–83 wt %, there exist (during melting or solidification) two components coexisting in two phases at constant atmospheric pressure. From the reduced phase rule[2] we see that such a system is univariant ($V = 2-2+1 = 1$). An analytical expression of univariance in a simple eutectic interaction is the van't Hoff freezing point relation for eutectic equilibria

$$-\ln N_A = \frac{\Delta H_A^\circ}{R}\left(\frac{1}{T} - \frac{1}{T_A^\circ}\right) \tag{1}$$

where, ΔH_A° = standard molar enthalpy of fusion; T_A° = freezing (or melting) point of species A at 1 atm total pressure; N_A = mole fraction of A in a mixture of A and B; T = freezing point of a mixture of A and B; and, R = gas constant. In evaluating ΔH_A° in eqn (1), values of T and T_A° were used corresponding to the final melting points in cyclical runs (*cf.* Table 3) (final rather than initial melting points were employed since, in general, the former were much easier to estimate than the latter). From a plot of $-\ln N_A$ versus reciprocal temperature (*cf.* Fig. 3), a value of $\Delta H_A^\circ \approx 33$ cal g^{-1} was calculated for RDX. This value is in good agreement with values previously reported[1], *i.e.*, 30 and 33 cal g^{-1} (Rogers[4] has indicated that a value of 35 cal g^{-1} has been reported for RDX). Further, utilizing a value of $T = 174$ °C (*cf.* RDX-22, 36), the lower value of the maximum solubility of HMX in RDX was calculated as *ca.* 48 wt % HMX; whereas, using a value of $T = 197$ °C (*cf.* RDX-20, 35), an upper value of the maximum solubility of RDX in HMX was estimated as *ca.* 83 wt % RDX. These values agree surprisingly well with experimental values. From values of the slope

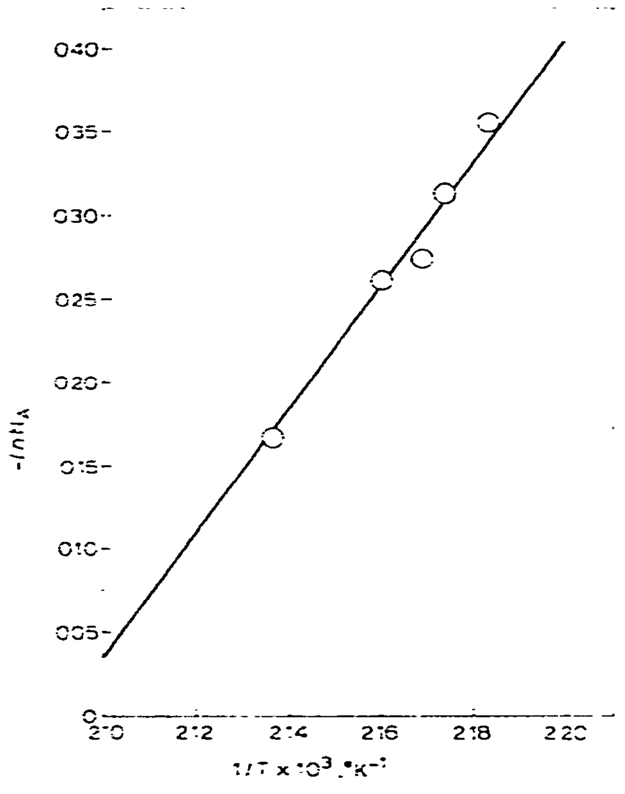

Fig. 3. Plot of $-\ln N_A$ versus reciprocal temperature.

and intercept obtained from the plot of Fig. 3, $T^{\circ}_{A} \approx 207$ °C (expt., 209–210 °C). It may also be mentioned here that the lower and upper limits of HMX and RDX solubility were occasionally checked in non-cyclic runs by employing neat RDX melting endotherm areas and neat HMX decomposition areas to estimate quantities of RDX and HMX, respectively, which had separated out.

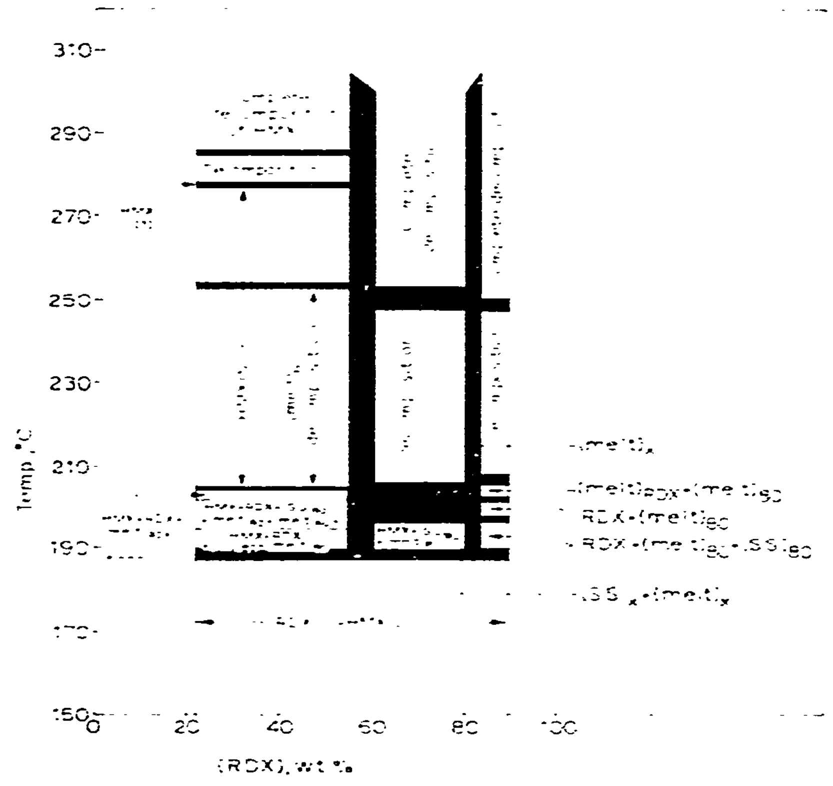

Fig. 4. Approximate heating only diagram (thermodynamic instability) for the melting and decomposition of RDX–HMX mixtures in still air.

Although values of the heat of decomposition (ΔH_{dec}) of RDX–HMX mixtures by DTA are only semi-quantitative, such values have been estimated and are reported in the following as a guide to a *possible* trend. Thus, for values of RDX contents equal to or less than 55 wt %, $\Delta H_{dec} \approx 0.5 \pm$ kcal g^{-1} (in this wt % range, values of ΔH_{dec} were based on the quantities of RDX and HMX used less the quantity of neat HMX, obtained from its decomposition exotherm; also, the ± sign indicates an average value). For an RDX range of *ca.* 55–82 wt %, $\Delta H_{dec} \approx 0.5 \pm$ kcal g^{-1}; whereas, for a range above 82 wt %, $\Delta H_{dec} \approx 0.8 \pm$ kcal g^{-1} (total weight of mixture used in these two ranges). In regard to these values of ΔH_{dec}, it may be mentioned that such values for neat RDX (m.p. ≈ 203 °C) have been reported[1] as *ca.* 0.5 kcal g^{-1}. However, Bohon[7] obtained an approximate value of ΔH_{dec} by DTA for RDX possessing a m.p. = 192 °C (this low melting point implies that the RDX may have been contaminated with 8–12% HMX[8]). He calculated a value of $\Delta H_{dec} = 0.77$ kcal g^{-1}. Values of activation energy (E) and apparent reaction order (n) for decomposition were also estimated for neat RDX and for mixtures of RDX–HMX. It was previously reported[1] that neat RDX possessed (in nitrogen or air) values of $E = 80 \pm$ kcal mole^{-1} and $n = 0.8 \pm$. For a mixture containing 82 wt % RDX, it was also reported[1] that $E = 66$ kcal mole^{-1} (a similar value was reported in the literature several times) and that $n = 0.7$ (these values were obtained from a run involving a non-cyclic program in air). Other compositions of RDX–HMX mixtures were thermally decomposed in still air using a heating only program. In the following are given, in order, wt % RDX, E in kcal mole^{-1}, and n: 89, 71, 0.8; 56, 66, 0.8.

Based upon non-cyclic data (initial thermodynamic instability obtained which was followed after the initial endotherm by presumably thermodynamic stable states) and cyclical heating runs (presumably thermodynamic stable states), an approximate tentative heating only diagram was constructed in Fig. 4 for the melting and decomposition of RDX–HMX mixtures in still air (*cf.* Table 3). As indicated earlier, RDX compositions were limited to 9–95 wt %. Limits of solubility were assumed to be 55–60 and 80–83 wt % RDX (*cf.* vertical shaded areas in Fig. 4). In this figure (and in Fig. 5), a question mark (or horizontal or vertical shaded area) denotes a region not

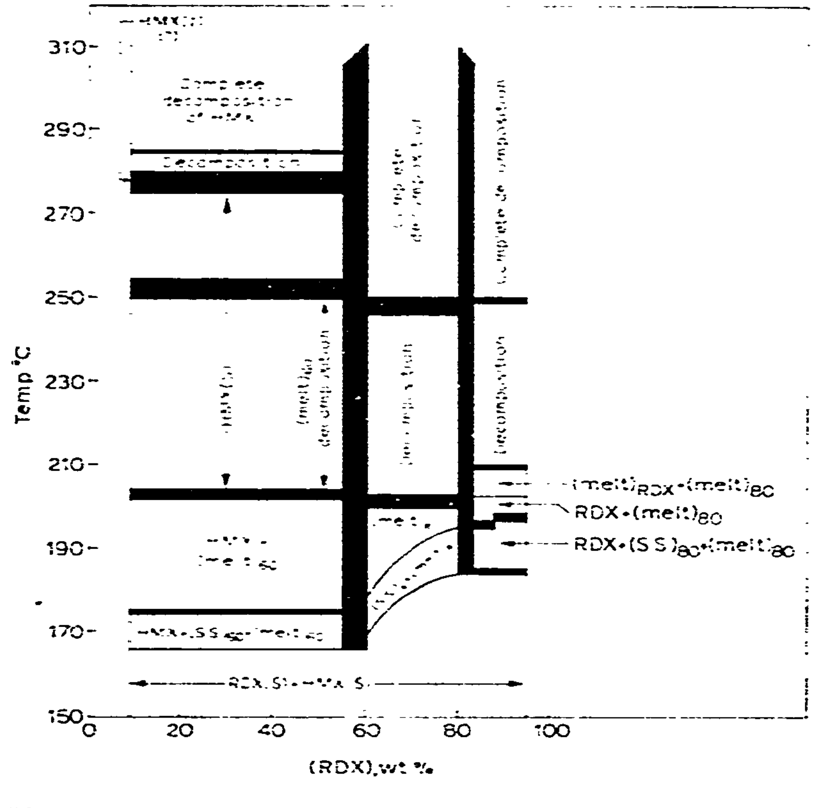

Fig. 5. Approximate diagram (thermodynamic stability) for the melting and decomposition of RDX–HMX mixtures in still air based on cyclical heating runs.

clearly demarcated by DTA alone: (l) and (S) denote liquid and solid phases, respectively; $(S.S.)_X$ consists of solid solutions of RDX–HMX between RDX values of *ca.* 55–83 wt % and where X = RDX content; $(S.S.)_{80}$ denotes a solid solution containing *ca.* 80–83 wt % RDX; $(melt)_{60}$ consists of a molten mixture of RDX–HMX containing *ca.* 55–60 wt % RDX; $(melt)_{80}$ comprises a molten mixture of RDX–HMX containing *ca.* 80–83 wt % RDX; and, $(melt)_X$ denotes a molten mixture of RDX–HMX between RDX values of *ca.* 55–83 wt % RDX and where X = RDX content. In Fig. 5 is depicted an approximate tentative diagram for the melting and decomposition of RDX compositions in still air based on cyclical heating runs (*cf.* Table 3). The diagram of Fig. 5 is better delineated than that of Fig. 4. Thus, in the latter figure, in the 60–80 wt % region, it is not clear at what temperature there is a separation between the $(melt)_X$ phase and the $[(S.S.)_X + (melt)_X]$ phase; further, at the lower RDX contents in Fig. 4, little can be stated regarding the separation and melting of RDX which ultimately leads to the formation of $(melt)_{60}$. That a non-equilibrium condition exists in regard to the separation of RDX at these lower contents can be seen from Fig. 5 and from a previous discussion.

ACKNOWLEDGMENT

The author wishes to express his gratitude to the following for their reviews and constructive criticisms of the manuscript: T. C. Castorina, S. Bulusu, K. Suryanarayanan, and H. Jackson.

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