

COMPATIBILITY OF POLYMERS WITH HIGHLY ENERGETIC MATERIALS BY DTA

LEO REICH*

Polymer Research Branch, Picatinny Arsenal, Dover, N. J. 07801 (U. S. A.)

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ABSTRACT

An areal method previously developed by the author for the estimation of kinetic parameters during polymer pyrolyses, *i.e.*, activation energy (E) and reaction order (n), was extended for the assessment of compatibility of various polymers with highly energetic materials by DTA. Thus, reproducible overall values of E and n were estimated for cellulose nitrate and cyclotrimethylene trinitramine and changes in values of these parameters were used as reliable indices for judging compatibility of highly energetic materials in various admixtures of polymers.

INTRODUCTION

The contact of a highly energetic material (HEM), *e.g.*, an explosive, with a relatively inactive material, *e.g.*, a plastic, may lead to a hazardous mixture, *i.e.*, there may be an unexpected increase in sensitivity and/or decrease in thermal stability of HEM. Various methods have been employed to test for such incompatibility.

A vacuum stability test has been used for compatibility testing^{1–3}. Some disadvantages of this method are: relatively large quantities of materials are required; the formation of condensable materials may be difficult to detect; relatively low temperatures are employed (*ca.* 100°C) so that slowly occurring reactions may be difficult to detect over the time interval used; relatively long test times are used (*ca.* 40 hr); etc. Rogers⁴ utilized a modified Henkin test to detect incompatibility in explosive mixtures. (The original Henkin test was largely abandoned when it failed to give correct values of activation energy of pure explosives.) Besides the preceding, TG and DTA techniques have been utilized to ascertain compatibility. This paper will be concerned with the latter technique.

Various workers have employed DTA techniques to test for compatibility of mixtures containing HEM. By this method may be estimated activation energy (E) and frequency factor (Z). In this connection, the Kissinger⁵ method has been widely used^{6–9}. Changes in values of E and Z for pure HEM and mixtures containing HEM may be used to ascertain compatibility. However, the Kissinger method has been

*Affiliate Professor of Chemistry, Stevens Institute of Technology, Hoboken, N.J., U. S. A.

criticized on several accounts. Thus, Rogers and Smith¹⁰ have indicated that the Kissinger equation,

$$\frac{E(\text{RH})}{RT_m^2} = Zn(1-X)_m^{n-1} e^{-E/RT_m} \quad (1)$$

where, (RH) = constant heating rate; n = reaction order; R = gas constant; T_m = absolute temperature at the DTA curve maximum; and X = fraction of material decomposed, can be employed to estimate E and Z from plots of $\log[(\text{RH})/T_m^2]$ versus $1/T_m$ only, strictly speaking, when $n = 1$. When a reaction is complex, X_m will vary with T_m at different values of (RH). Another disadvantage of this method is that several DTA traces are required in order to employ Eqn. (1) and at the higher heating rates, dynamic thermal equilibrium becomes more difficult to attain. Besides Eqn. (1), another often used expression is

$$E = R \frac{\ln(d_1/d_2)}{\left(\frac{1}{T_2} - \frac{1}{T_1}\right)} \quad (2)$$

where, d_1 and d_2 denote any two distances from the baseline at the corresponding absolute temperatures, T_1 and T_2 . Thus, Rogers and Morris¹¹ used Eqn. (2) to estimate values of E for various explosives. However, in using Eqn. (2), it is assumed that $n = 0$. From the preceding, it can be seen that the estimation of kinetic parameters, E , n , and Z , from Eqns. (1) and (2) involves assumptions which may be erroneous for the system used. Besides being used to evaluate kinetic parameters, DTA techniques may be employed to detect incompatibility by observing the shifting of exothermic peak temperatures to lower temperatures when comparing HEM and mixtures containing HEM⁹. While this shift may be an important criterion of incompatibility, some systems may exist wherein such a shift may be small even though values of E (and n) may change appreciably (see Results and Discussion). Relatively recently, Reich¹²⁻¹⁴ presented an areal method for estimating overall values of E and n for polymer degradations using a single DTA thermogram. In this method, various expressions involving E and n were developed and are listed in the Theory section which follows. (This method assumes $1 \gg 2RT/E$ (or that $1 - 2RT/E \approx \text{constant}$) which is generally valid for HEM.)

THEORY

In the Reich method, the following expressions were developed (expressions for $n = 1$ are not listed since these are not used in this paper)

$$F(T) = \left(\frac{\bar{a}_1}{\bar{a}_2}\right)^n \left[\frac{1 - (\bar{a}_1/A)^{1-n}}{1 - (\bar{a}_2/A)^{1-n}} \right], n \neq 1 \quad (3)$$

where

$$F(T) = (T_1/T_2)^2 (\Delta T_1/\Delta T_2), \text{ and,}$$

$$E/R = [(1-n) T^2 \Delta T/A] / (\bar{a}/A)^n [1 - (\bar{a}/A)^{1-n}], \quad n \neq 1 \quad (4)$$

In Eqns. (3) and (4), ΔT denotes the height of the DTA (or DSC) curve;

$$\bar{a} = \int_T^\infty \Delta T dT; \quad A = \int_{T_1}^\infty \Delta T dT.$$

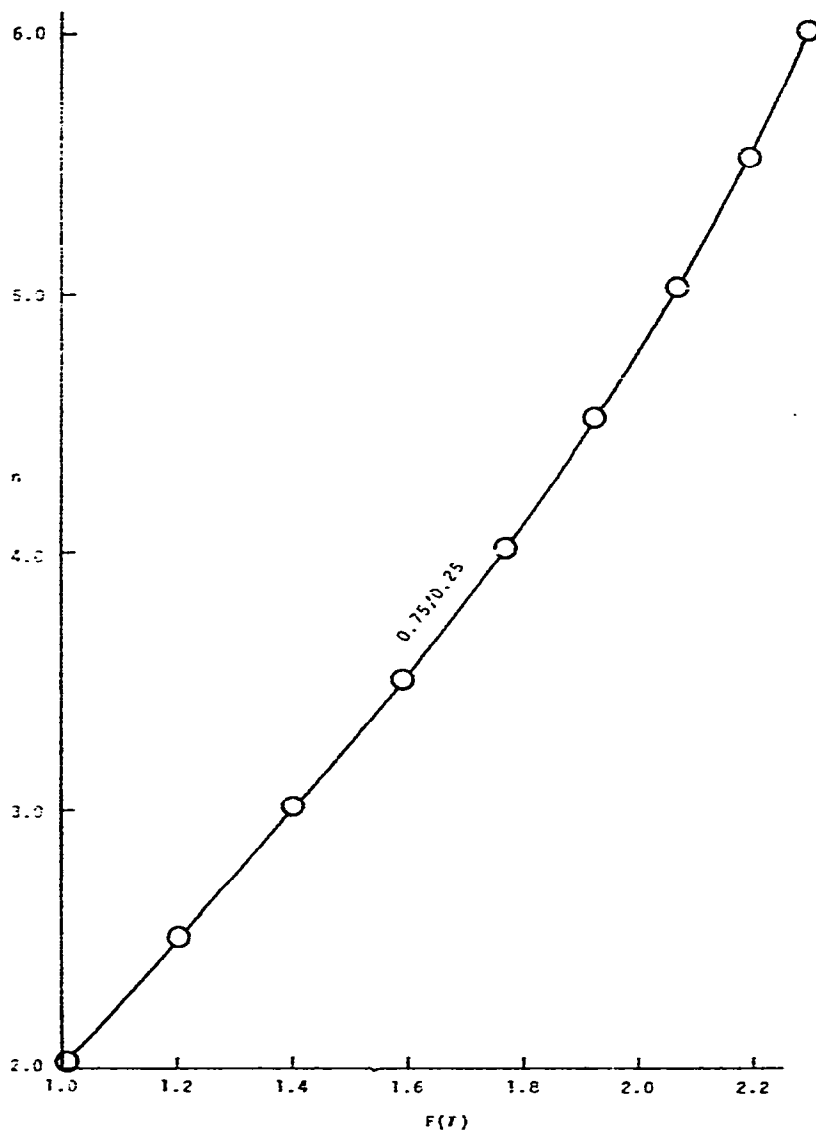


Fig. 1. Plot of reaction order n versus $F(T)$ for the ratio $(\bar{a}_1/A)/(\bar{a}_2/A) = 0.75/0.25$ for values of n ranging from 2 to 6.

Prior to obtaining E from Eqn. (4), it is necessary to estimate n . From Eqn. (3), it can be seen that $F(T)$ may be plotted against n for various values of \bar{a}_1/A and \bar{a}_2/A . Such plots were constructed for various values of the ratio $(\bar{a}_1/A)/(\bar{a}_2/A)$ for values of n ranging from 0 to 2^{12-14} . However, in this paper it was necessary to extend the range of n using a ratio (arbitrary) of 0.75 to 0.25. In Fig. 1 is depicted a plot of $F(T)$ versus n for the ratio, 0.75/0.25, with the values of n ranging from 2 to 6. Values of the sample temperature T and the height of the thermogram ΔT were obtained where \bar{a}/A possessed the desired value on the thermogram. In obtaining values of areas, a weighing method was used. After a few rapid trial-and-error weighings, the sample temperature and peak height corresponding to the ratio \bar{a}/A could be readily obtained. From these values of ΔT and T , $F(T)$ could be calculated and consequently values of n could be estimated from Fig. 1 (or a related figure containing values of n of 0 to 2). After determining the value of n , a value of E could be calculated from Eqn. (4).

The above method was applied to mixtures of various polymers and HEM. The results obtained by this method are the subject of this paper. It may be remarked here that this method was applied to DTA traces of polymer pyrolyses as well as to data obtained for the decomposition of benzenediazonium chloride in aqueous solution¹³. Rather good agreement was generally obtained between kinetic parameters, E and n , calculated by this method and corresponding values, reported in the literature (which generally employed other techniques and/or methods of calculation). This agreement indicates that the method utilized in this paper should afford reliable overall values of E and n . (It should however be noted here that a "Boersma-type" DTA apparatus was previously employed¹³ whereas, in this paper, "classical" DTA is used.)

EXPERIMENTAL

Starting materials

Polymer powders admixed with HEM were: Teflon, duPont (T); polyethylene, duPont DTA grade (PE); polystyrene, Ar Ro Labs., Inc., $M_w = 51,000$ (PST); Epon 828 (nadic anhydride cured); Epon 828 (BF₃-amine cured); polyacrylamide, Borden Chemical Co. (PAA); polymethyl-methacrylate, (with strong odor) (PMMA); polyisobutylmethacrylate, Rohm & Haas (PIMA); polyethylmethacrylate, (with strong odor) (PEMA); Gantrez AN-139, General Aniline & Film Corp. (copolymer of methyl vinyl ether and maleic anhydride); poly-n-octadecylacrylate, Frankford Arsenal (PODA).

The highly energetic materials used were: cellulose nitrate (CN), 12.2% nitrogen (courtesy of E. Turngren); cyclotrimethylene trinitramine (RDX), m (onset) = 202°C, recrystallized from acetone and γ -butyrolactone (courtesy of J. R. Autera); cyclotetramethylene tetranitramine (HMX), β -polymorph, 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), aluminum oxide, and high purity nitrogen.

Apparatus

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

Procedure

In the case of CN, 1.4 to 3.0 mg of CN were admixed with 1.0 to 5.0 mg of polymer and 10 to 17 mg of alumina were placed above the admixture. For RDX, 2.0 to 2.7 mg of RDX were admixed with 1.8 to 4.8 mg of polymer and 15 to 20 mg of alumina were placed above the admixture. The Chromel-Alumel thermocouple tip was inserted into the admixtures and alumina (*ca.* 19 mg) was used as the reference material. Approximately 2 cfh of nitrogen gas was admitted for each run. A heating rate of 6°C/min was employed throughout. The admixing was accomplished using a fine metal wire.

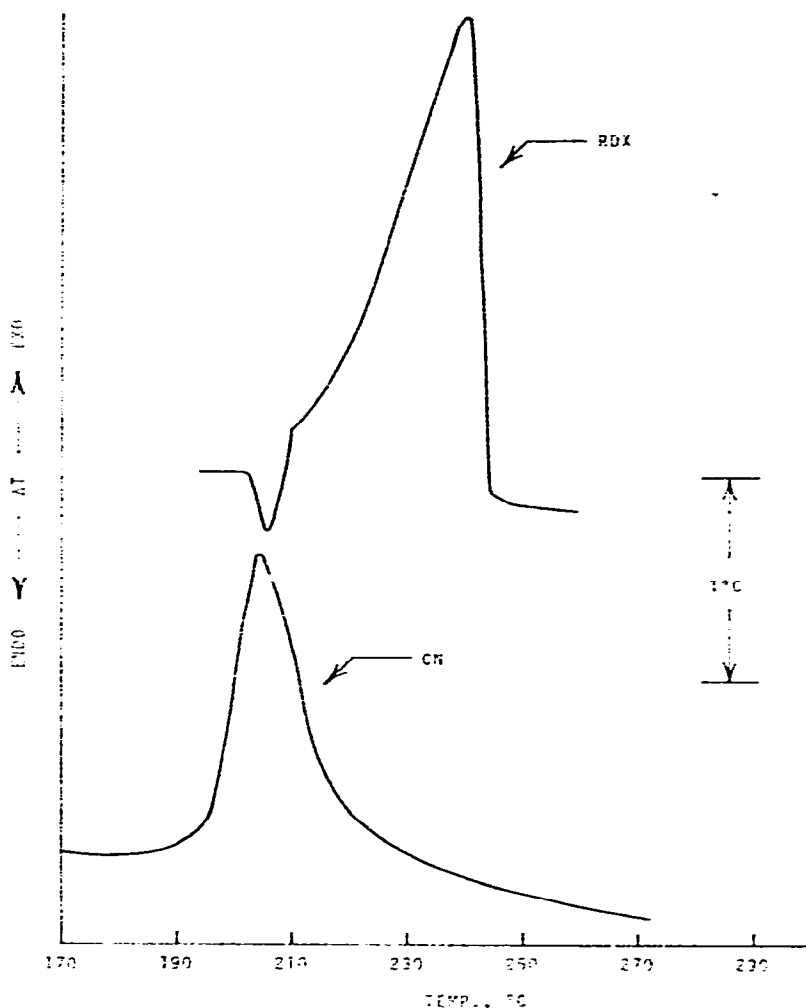


Fig. 2. DTA thermograms for cellulose nitrate (CN, 2.0 mg) and cyclotrimethylene trinitramine (RDX, 2.2 mg); heating rate = 6°C/min.

TABLE I
SUMMARY OF COMPATIBILITY DATA FOR CELLULOSE NITRATE AND CYCLOTETRAMETHYLENE TRINITRAMINE

Run no.	HEM	Polymer	Wt. % HEM	Decomposi. peak temp. (°C)	η	i (kcal mole ⁻¹)	ΔH_{400} (kcal g ⁻¹)	ΔH_f (cal g ⁻¹)
CN-1	cellulose nitrate ↓ RDX ↓	—	100	204	4.6	180	0.40	—
CN-2 to 6		T	32-75	203-206	5.0±	187±	0.37±	—
CN-7 to 10		PE	34-50	204-208	4.8±	170±	0.38±	—
CN-11 to 12		PST	38-48	204-205	4.7±	177±	0.33	—
CN-13		Epon 828 (anh. cured)	35	205	4.4	170	0.42	—
RDX-1,1B		—	100	240	0.8±	80±	0.49	30±
RDX-2		PE	42	237	0.7	81	0.25	20
RDX-3,3A		Epon 828 (anh. cured)	42	220±	1.9±	107±	0.54±	—
RDX-4		Epon 828 (anh., extracted)	43	—	—	—	—	8
RDX-4A		Epon 828 (anh., extracted)	42	224	1.7	105	—	6
RDX-5		PST	47	241	0.9	84	0.51	23
RDX-6		Epon 828 (BF ₃ -cured)	33	238	0.8	79	0.52	29
RDX-7		PAA	51	241	0.8 _g	88	0.65	33
RDX-8	PMMA	47	239	1.1 _s	66	0.58	—	
RDX-9	PIBM	54	237	1.0	76	0.48	20	
RDX-10	PEMA	38	238	1.3 _h	70	0.66	—	
RDX-11	Gantrez	55	219	—	—	—	—	
RDX-12	PODA	53	238	0.6	76	0.48	22	
RDX-13	(HMX)	82	245	0.7	66	—	16	

In order to ascertain the effect of the polymeric substances upon CN and RDX, it was necessary to obtain thermograms on these latter materials alone. Values of E and n were calculated for CN and RDX and compared with corresponding values for admixtures of these HEM. When relatively large differences in E and n were found, thermograms were obtained for the polymeric material alone in order to ascertain that there were no endotherms or exotherms in the temperature range of interest (170–270°C for CN and 195–250°C for RDX). A thermogram was also obtained for alumina alone. In Fig. 2 are depicted thermograms for CN and RDX alone. Peak temperatures for all runs were also noted (*cf.* Table I).

The thermocouple temperatures were calibrated in the temperature range of interest by using tin and indium standards. Further, these standards (along with zinc) 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) (*cf.* Table I).

RESULTS AND DISCUSSION

The various results obtained for CN and RDX are summarized in Table I. From this table, it can be seen that overall values of E and n for RDX alone (*cf.* RDX-1, 1B) are, respectively, $80 \pm$ kcal mole⁻¹ and $0.8 \pm$ (the \pm symbol indicates an average value). Also, from Fig. 2, it can be seen that a distinct endothermic melting point peak occurs prior to the strong exothermic decomposition peak. Values of ΔH_{dec} and ΔH_f obtained from such peak gave the following corresponding values, 0.49 kcal g⁻¹ and 30 cal g⁻¹ (these values should only be considered as semi-quantitative since such values may depend upon thermocouple tip location in the sample, changes in thermocouple tip characteristics from run to run, etc.; nevertheless, these values are given to indicate *possible* trends). In this connection, it may be remarked that a Perkin-Elmer Model DSC-1B scan of the thermal decomposition of a sample of RDX at a heating rate of 10°/min in nitrogen afforded¹⁵ $\Delta H_{dec} = 0.47$ kcal g⁻¹ and $\Delta H_f = 33$ cal g⁻¹ (based upon the decomposition area). (However, results obtained by DSC appeared to depend upon the method of RDX encapsulation used¹⁵.) However, the values of E and n calculated in this work appeared to be at variance with reported literature values. Thus, using DSC techniques, Rogers and Morris¹¹ obtained $E = 67.4 \pm 3.0$ kcal mole⁻¹ from Eqn. (2). (The limitation of this equation has already been mentioned, *i.e.*, $n = 0$.) Utilizing another expression, Rogers and Smith¹⁰ calculated $E = 52$ kcal mole⁻¹ and $n = 1.3$ between 10 and 80% conversion; at higher conversions, the value of E rose to over 176 kcal mole⁻¹ (thus, the overall value of E would be expected to be much higher than 52 when RDX decomposition is carried out to complete conversion, as in the present work). Batten and Murdie¹⁶ studied the thermal decomposition of RDX in nitrogen using gasometric techniques and arrived at a value of $E = 63$ kcal mole⁻¹ for the sample in a *spread condition* and for temperatures below the melting point (equal to or less than 198°C). Others¹⁷ have also employed gasometric techniques to obtain a value of

$E = 47.5 \text{ kcal mole}^{-1}$ (assuming that $n = 1$). Nevertheless, values of $E = 80 \pm$ kcal mole⁻¹ and $n = 0.8 \pm$ have been consistently obtained in this work. (It may be noted here that whereas DTA may at best be only semi-quantitative for estimating values of ΔH_{dec} and ΔH_f since these values depend upon areas and these areas may not be reproducible from time-to-time, values of E and n are dependent primarily upon the shape of the exothermic (or endothermic) curve obtained and are therefore not subject to the variations that may be encountered with values of ΔH_{dec} and ΔH_f and are hence more reliable values.) Since a common contaminant of RDX is HMX, a run was carried out (*cf.* RDX-13) wherein RDX was thermally decomposed in the presence of HMX. The value of E dropped to *ca.* 66 kcal mole⁻¹ and that of n to *ca.* 0.7.

At any rate, employing the reproducible values obtained in RDX-1, 1B, it can readily be seen that pronounced changes in E and n occurred when RDX was admixed with Epon 828 (anh. cured) (*cf.* RDX-3, 3A) or with Gantrez (*cf.* RDX-11). In the latter case, the exotherm was so strong that the recorder pen moved off the chart so that no values of kinetic parameters could be obtained. However, the exothermic peak temperature dropped from 240 to *ca.* 219°C and only a small melting endotherm could be seen. Similarly, in the presence of anhydride-cured Epon 828, values of E and n changed drastically from 80 to 107 and 0.8 to 1.9, respectively. Further, the peak temperature dropped from 240 to 220°C and the melting endotherm virtually disappeared (*cf.* Fig. 3). In this regard, it may be mentioned that extraction of the anhydride-cured Epon 828 with acetone (RDX-4) and subsequently with acetone and benzene (RDX-4A) resulted in the reestablishment of a distinct melting endotherm. However, values of ΔH_f were relatively low and values of E , n and peak temper-

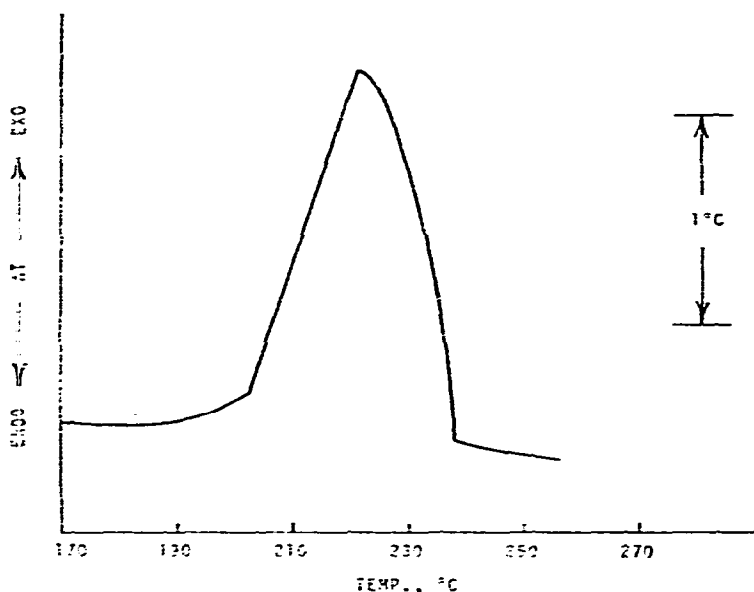


Fig. 3. DTA thermogram for an admixture of RDX (2.5 mg) and Epon 828, anh. cured (3.4 mg); heating rate = 6°C/min.

ature were still at great variance with values for RDX alone. A thermogram obtained for the anhydride-cured Epon 828 alone did not reveal any peaks in the temperature range of interest. In view of these results and since Gantrez contains maleic anhydride moieties, it is apparent that anhydride groups caused the incompatibility observed. (Because of the large variation in E and n , a strong chemical interaction between anhydride moieties and RDX may have occurred.) In this connection, it may be noted here that Epon 828 (BF₃-cured), which should not contain anhydride groups, was compatible with RDX (*cf.* RDX-6).

Other materials appear to be "borderline" as far as being compatible with RDX is concerned. Thus, the PMMA and PEMA samples appeared to be incompatible with RDX, the value of E dropping to 66 and 70 and that of n rising to 1.1₅ and 1.3₈. Despite these changes, the peak temperature did not change much indicating that peak temperature values may, by themselves, not be a reliable measure of compatibility. In regard to PMMA and PEMA, it should be remarked that these materials possessed strong odors. Such odors were much less apparent in the acrylate samples, PIBM (RDX-9) and PODA (RDX-12). While there were changes in E and n for these materials, they were not as severe as for PMMA and PEMA. Thus, it is likely that contaminants in acrylate samples, rather than the polymer functional groups themselves, were responsible for any incompatibility observed. Finally, PE, PST, Epon 828 (BF₃-cured), and PAA appeared to be compatible with RDX. (Vacuum stability tests have indicated that PE is compatible with RDX³. However, these tests also indicated compatibility of RDX with a sample of Epon 828 (anh. cured) used in runs RDX-3,3A.)

As in the case of RDX, kinetic parameters, E and n were employed to assess compatibility of CN with various polymers. From Fig. 2, it can be seen that the thermograms for RDX and CN are quite different. Thus, in the former case, a melting endotherm was observed whereas this was not observed for CN. Further, in the case of RDX, the onset of decomposition occurred relatively slowly and after the peak temperature was reached (*ca.* 240°C), a rather sharp drop in ΔT was noted. On the other hand, the onset of CN decomposition occurred comparatively rapidly and after a peak temperature was attained (*ca.* 204°C), a rather mild decline in ΔT was observed. Thus, the mechanisms of RDX and CN decomposition would be anticipated to be quite different. In this connection, $n(\text{RDX}) = 0.8$ while $n(\text{CN}) = 4.6$ (*cf.* Table I) indicating that the CN decomposition involves a much more complex mechanism than the RDX decomposition¹⁰. Further, a value of $E = 180 \text{ kcal mole}^{-1}$ was calculated for CN. (While literature values of E are generally much lower, the temperatures and techniques employed in attaining these values were different, *e.g.*, gasometric methods¹⁸. Nevertheless, the values reported in this paper are reproducible.) From Table I, it is apparent that T, PE, PST, and Epon 828 (anh. cured) are compatible with CN.

From Table I, a trend in regard to values of ΔH_{dec} and ΔH_f and compatibility may be apparent. Thus, for CN, compatibility was noted for various polymeric admixtures, and the values of $(\Delta H_{\text{dec}})_{\text{av}} = 0.38 \pm \text{kcal mole}^{-1}$ which is in excellent

agreement with $\Delta H_{dec}(\text{CN}) = 0.40 \text{ kcal mole}^{-1}$. For RDX, such a trend was not definitive. (This may, in part, be due to the sensitive nature of RDX decomposition¹⁶.) Thus, whereas compatible materials, *e.g.*, Epon 828 (BF_3 -cured) and PST possessed values of $\Delta H_{dec} = 0.51\text{--}0.52 \text{ kcal mole}^{-1}$ as compared with $\Delta H_{dec}(\text{RDX}) = 0.49 \text{ kcal mole}^{-1}$, other compatible materials either afforded lower or higher values. In this regard, $\Delta H_{dec}(\text{PAA}) = 0.65 \text{ kcal mole}^{-1}$ and $\Delta H_{dec}(\text{PE}) = 0.25 \text{ kcal mole}^{-1}$. Where incompatibility with RDX was observed, values of ΔH_{dec} were generally greater than $0.49 \text{ kcal mole}^{-1}$. Further, when incompatibility with RDX occurred, values of ΔH_f were generally much lower than the $\Delta H_f(\text{RDX})$, *cf.* RDX-4, 4A, 13. (This may be indicative that the incompatibility causes a decrease in the order of the crystal lattice of RDX.) However, it should also be noted here that ΔH_f was lower than anticipated even for compatible materials, although not as low as for incompatible materials.

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