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Microcalorimetry and DSC study of the compatibility of energetic materials

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Abstract

This study included accelerated aging of cyclotetramethylene tetranitramine (HMX) and CH-6 (>97% RDX), coating of HTPB propellant with two sealants (A, B) and reaction kinetics between cyclotrimethylenetrinitramine (RDX) and organic salt (ammonium benzoate). Isothermal microcalorimetry (IMC) analyses at 55–75°C and DSC analyses at decomposition temperatures (180–300°C) were in agreement regarding compatibility. IMC heat flow measurements indicated that aging conditions did not affect HMX and CH-6. DSC rates of reaction at 200°C were similar and thus indicated no reaction. DSC onset of reaction and IMC heat flow measurements showed that one sealant (A) had an interaction with the HTPB propellant while the other did not. When the sealants were combined their reaction with HTPB decreased as the amount of sealant B increased. Reruns of HTPB with sealants A and sealants A + B after 3 weeks at room temperature showed that there was still an additional reaction of ~9%. IMC and DSC kinetic analyses were carried out on HTPB propellant + sealant A admixture. IMC gave a value of 5 kcal/mol for the reaction in the 55–75°C region while DSC measured the decomposition reaction where the activation energy was lowered from 48 kcal/mol for the propellant to 43 kcal/mol for the admixture. DSC kinetic study of RDX + organic salt showed a shift of the RDX peak temperature from 217°C (neat RDX) to 180°C (admixture). The activation energy for decomposition of the admixture was 25 kcal/mol. Literature values for neat RDX is 47 kcal/mol. Thus DSC kinetic data indicated that the admixture was incompatible at elevated temperature. An IMC kinetic study at temperatures from 65 to 77°C for this admixture gave a value of 33 kcal/mol. The reaction mechanism in the DSC and IMC experiments may be different since in the former case it involves a reaction between a gas (NH_3) and a liquid (RDX) while in the latter case it involves a gas (NH_3) and solid RDX which is a much slower reaction as also reflected in the higher activation energy.

Keywords: Microcalorimetry; Cyclotetramethylene tetranitramine; Cyclotrimethylenetrinitramine

1. Introduction

Compatibility studies of energetic materials by DSC and TG have been carried out in our laboratory [1–7] for several years. In order to detect any interaction between the ingredients, the temperature had to be raised to about 50°C of the decomposition peak temperature. The heat flow sensitivity scale in DSC was at least 100 mW/g. The major advantages of the isothermal microcalorimetry (IMC) method are (a) the heat flow sensitivity scale is now in the microwatts (μW) and nanowatts (nW) region, (b) a large sample mass up to 30 g depending upon the sensitivity of the sample, (c) temperature measurements in the 40–70°C region, (d) kinetic studies in this temperature region may result in more realistic service life predictions for propellants because you would not have to be concerned upon changes in mechanism as when you extrapolate from high temperature DSC

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measurements to temperatures in the 40–70°C region and (e) accurate constant temperature experiments may be performed. In the present study good agreement was observed in the conclusions drawn from DSC and IMC experiments on compatibility of energetic materials.

2. Experimental

DSC experiments were carried out with a TA Instrument Model 2910 DSC module and a 3100 Thermal Analyzer. Sample masses varied from 0.5 to 3 mg and were placed in aluminum sample pans. Admixture ratios were 1:1. The variable heating rate method employed heating rates of 0.5, 1, 2, 5, 10 and 20°C/min in a nitrogen atmosphere. The instrument was calibrated with indium.

A Calorimetry Science Corporation (CSC) 4400 IMC and two 4500 INC instruments were employed. The instruments were calibrated according to the manufacturer procedure. The IMC was held at 55–75°C with sample masses of ~5 g hydroxyl terminated polybutadiene (HTPB) propellant and ~0.4 to ~0.9 g of sealants. Sealant A (major ingredient is lead peroxide) and sealant B (major ingredient is polysulfide) were mixed in ratios of 1:1 and 1:10 (A:B). The ~5 g HTPB propellant was cut into ~25 slices and coated with the sealant (s) and then placed inside a 30 ml glass bottle. Later it was found to be more efficient to put the liquid sealant inside the bottle and then add propellant to it and mix the ingredients together. Since sealant A was the reactive ingredient whenever it was used the joule value was normalized to a constant value of sealant A (i.e., 0.6 g). The bottles were capped. INC experiments were carried out at three temperatures namely 65.7, 70.7, and 76.8°C. Sample masses varied from 0.1 to 0.4 g and were placed in 2 ml glass vials and capped. Samples included cyclotetramethylene tetranitramine (HMX), cyclotrimethylenetrinitramine (RDX), CH-6 whose major ingredient (>97%) is RDX, and ammonium benzoate (AB). Admixtures of RDX and AB were prepared in molar ratios of 2:1, 1:1, and 1:2 and since AB was the reactive ingredient the enthalpy values are reported as J/g AB.

Before any sample is run in the microcalorimetry it is run in the DSC and TG instruments at 5°C/min in order to see where the decomposition temperatures occurred. Then the samples are run for 20 h at 80°C to see if any exothermic events and weight loss occurred. The magnitude (i.e., mW/g per %wt loss) of the interaction if any would determine whether the samples would be run in the microcalorimeter and under what conditions (i.e., sample mass and temperature).

3. Discussion

3.1. *Aging of HMX and CH-6 (>97% RDX) accelerated*

Samples of HMX and CH-6 were aged at 50% RH/40°C/mol. DSC kinetic analyses employing a variable heating rate method [8] were carried out in a sealed and open sample pan and the results compared to isothermal microcalorimetry analysis at 70°C for 100 h. Figs. 1 and 2 for unaged HMX in an open pan and for aged HMX in sealed pans, respectively, showed differences in the peak shape, rate and enthalpy of reactions while peak maximum were within ±1°C. Higher values were observed when the decomposition gases were confined. Similar observations were noted for CH-6. Rate constants for decomposition at 200°C were calculated and they were similar for aged and unaged samples namely $0.0002 \pm 0.0001\ \mathrm{min}^{-1}$ for HMX and $0.005 \pm 0.001\ \mathrm{min}^{-1}$ for CH-6. Thus aged and unaged samples were the same and accelerated aging did not have any effect.

Microcalorimetry analyses of unaged/aged samples showed heat flow values in microwatts were close to zero which indicated that no reaction occurred in the aged samples. The IMC and DSC data were in agreement.

3.2. *HTPB propellant coated with sealants*

HTPB is a hydroxylterminated polybutadiene polymer cross-linked with an epoxide with fillers such as oxidizer (major ingredient), fuel, plasticizer, etc. The propellant is coated with a mixture of sealants. Namely, sealant A (major ingredient is lead peroxide) and sealant B (major ingredient is polysulfide). In a 30 ml bottle neat propellant (~5 g) and sealants (~0.6 g) were run and then combinations of propellant with sealants were carried out at isothermal

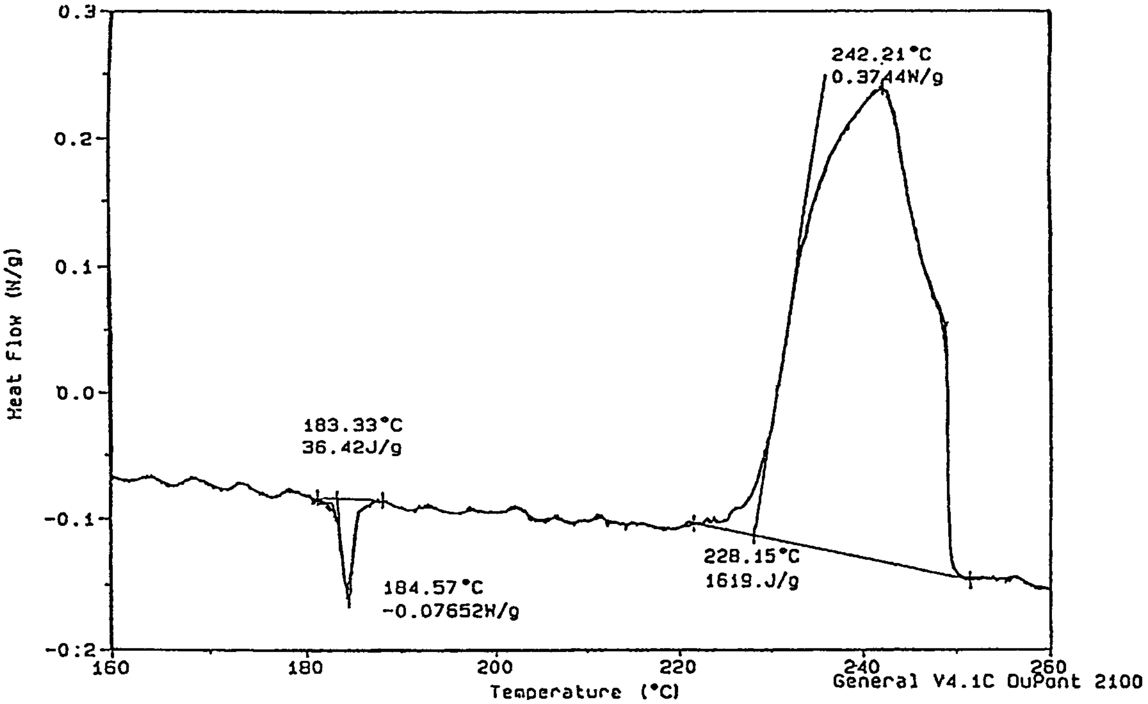

Fig. 1. DSC curve of unaged HMX in an open pan at 0.2°C/min.

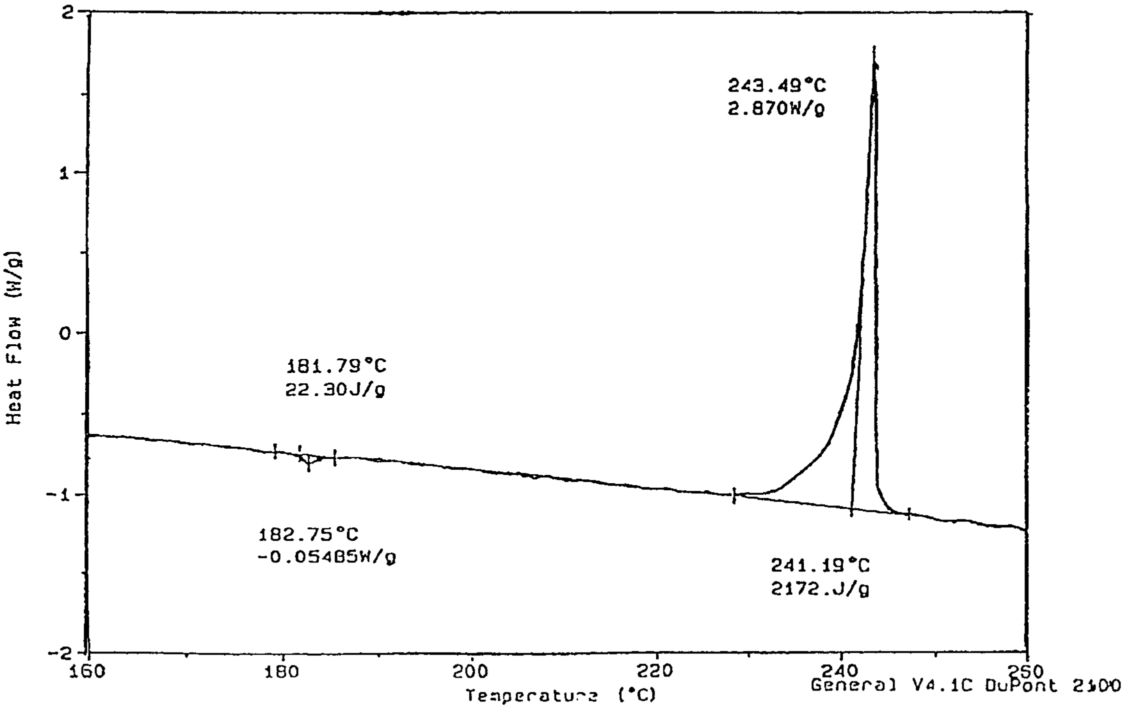

Fig. 2. DSC curve of aged HMX in an open pan at 0.2°C/min.

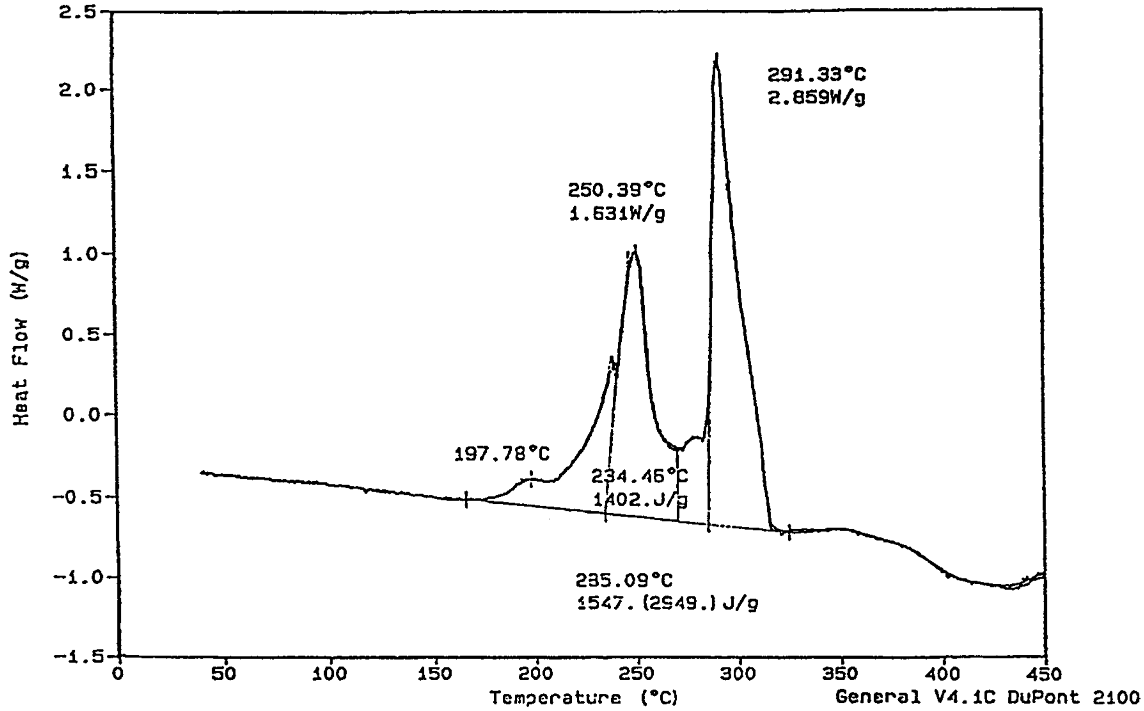

Fig. 3. DSC curve of HTPB propellant in sealed pan at 2°C/min.

temperatures of 55–75°C for at least 100 h. DSC analyses in open sample pans in a nitrogen atmosphere were also done.

The sealants had transitions in the same temperature region where the decomposition of the oxidizer occurred. DSC curve of the propellant is shown in Fig. 3. Addition of sealant A to HTPB showed the onset of decomposition to be shifted to a much lower temperature (~130°C) which indicated an interaction between them. With sealant B the reaction was insignificant.

Microcalorimetry curves of neat propellant, neat sealant B and propellant + sealant B had heat flow values near zero which indicated no reaction was occurring in these samples. The IMC curve in microwatts for sealant A is presented in Fig. 4, the decrease in microwatts from ~750 to ~50 with time was typical for an *n*th-order reaction. Integration of this curve is shown in Fig. 5 where a plot of joules versus time gradually is leveling off after 75 h at 70°C.

Integral plots (joules versus time) were obtained for admixtures of sealants A + B, HTPB + sealant A, and HTPB + sealants A + B (1:1), respectively. The data are presented in Table 1 and plotted as a bar graph in Fig. 6. It is evident that the admixture of HTPB propellant and sealant A is incompatible because the enthalpy of reaction for the admixture is greater than the sum of the reactants, i.e., 64 J > 33 J (sealant A) + 0 J (HTPB). The greater the difference, the greater the degree of incompatibility. Compatibility of energetic materials by microcalorimetry has been expressed by two equations, namely

$$C_{ab} = \frac{2E_{ab}}{E_a} + E_b \qquad (1)$$

$$C_{ab} = 2E_{ab} - \frac{E_a + E_b}{2} \qquad (2)$$

where E is the energy evolved in J/g, C the compatibility, subscripts a and b refer to the individual components and subscript ab refers to the mixture of a and b. In Eq. (1) [9], if $C \leq 2$ then the mixture is compatible and if $C > 3$ then it is incompatible. In

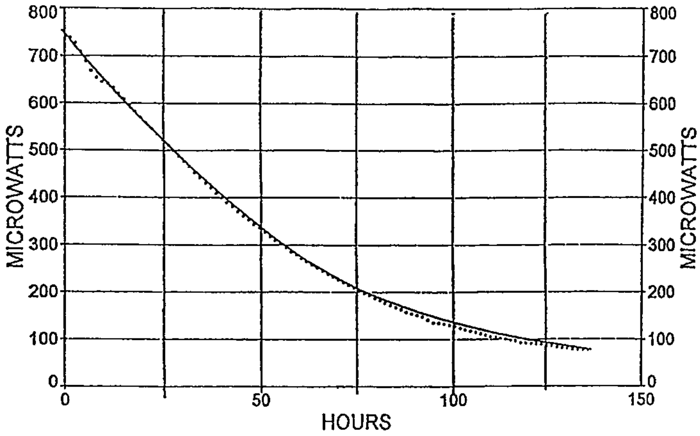

Fig. 4. IMC curve in a microwatts of sealant A at 70°C.

our case

$$C_{ab} = \frac{2 \times 64}{0 + 33} = 3.9\,\mathrm{J/g}$$

The admixture is *incompatible*. Using Eq. (2) [10]

$$C_{ab} = 2 \times 64 - \frac{0 + 33}{2} = 47.5\,\mathrm{J/g}$$

Therefore, the compatibility of HTPB propellant with sealant A was found to be 47.5 J/g.

The higher the number the greater the degree of incompatibility. When the admixture is HTPB + AB (1:10) then $E_{ab} = -3$ (see Table 2), E_a for HTPB = 0, E_b for A : B (1 : 10) = −4. Therefore,

$$C_{ab} = \frac{2 \times -3}{0 + -4} = 1.5$$

and the admixture is *compatible*.

Three samples of HTPB + sealant were rerun after being at room temperature for 3 weeks. The integral plot of the rerun sample Fig. 7 showed an enthalpy value of about 6 compared to a value of 52 in the initial run. The rerun data are also given in Table 1 and plotted as a bar graph in Fig. 8 in comparison to the initial run. It appears that the reaction between the propellant and sealant was about 90% completed in

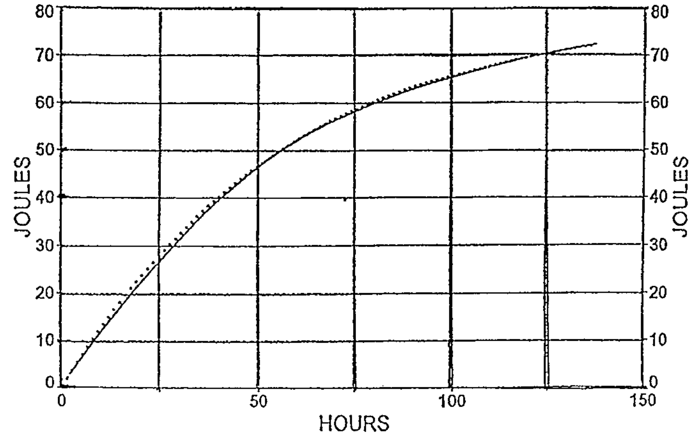

Fig. 5. IMC curve in joules of sealant A at 70°C.

Table 1
Microcalorimetry data after 70 h at 70°C for the HTPB propellant and sealants A and B

Mass (g)				Energy enthalpy, J/0.6 g (A)
HTPB	A	B	A + B[a]	
3.0				0
		0.834		−3.3
		0.91		−2.2
5.171		0.9066		−3.3
5.055		0.8155		−3.6
3.02	0.53			60
5.01[b]	0.622			66
	0.559			38
	0.498			28
			0.8531	37
	0.784	0.756		42
			0.855	31
5.1825			0.910	52
5.076	0.420	0.412		56
5.127	0.5299	0.5324		52
Return[c] after 3 weeks at room temperature				
5.01[b]	0.622			7
5.1825			0.910	6
5.076	0.420	0.412		4

[a] Ratio of A:B is 1:1.

[b] Sample covered with 20 g of sea sand.

[c] Appears about 9 ± 2% additional reaction.

Table 2
Microcalorimetry data for HTPB propellant with sealants A and B in the ratio of 1:10

Mass (g)			Energy enthalpy, J/0.6 g (A)
HTPB	A	A + B[a]	
5.64	0.637		64
5.159	0.698		67
		0.989	−4[a]
5.064		0.985	−3[a]
5.183		0.985	−3[a]

[a] Energy value based on total mass of A + B.

the initial run. The ratio of sealant in the IMC and DSC work was 1:1 (A:B). In actual practice the ratio is 1:10 (A:B). Since sealant B does not react with HTPB at 70°C/70 h the 1:10 ratio of A:B would be expected to have only minimal reaction due to dilution by sealant B in the admixture. IMC data for HTPB with sealant in 1:10 ratio (A + B) are given in Table 2 and confirmed expectation of minimal reaction.

An IMC kinetic study was made of the HTPB propellant + sealant A at temperature from 55 to 75°C. The kinetic plot is displayed in Fig. 9. Activation energy of 5 kcal/mol was calculated for the

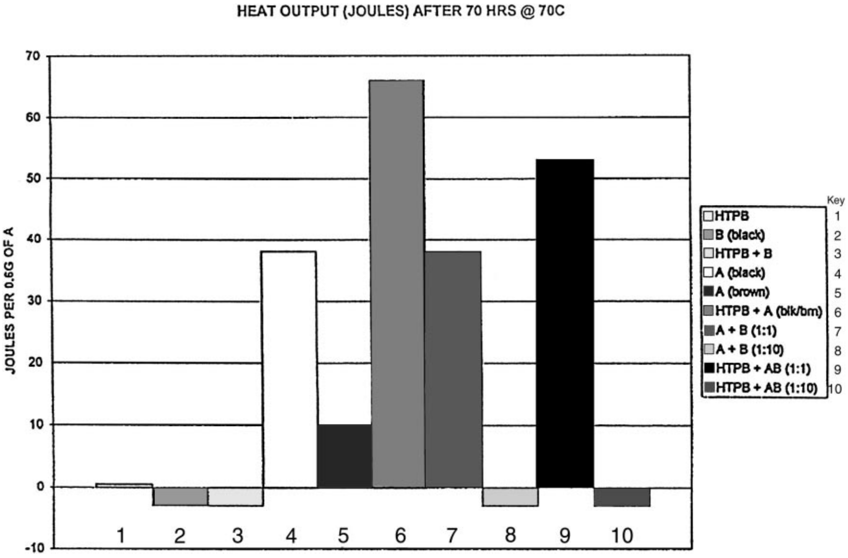

Fig. 6. IMC bar graph plot of HTPB propellant and sealants at 70°C.

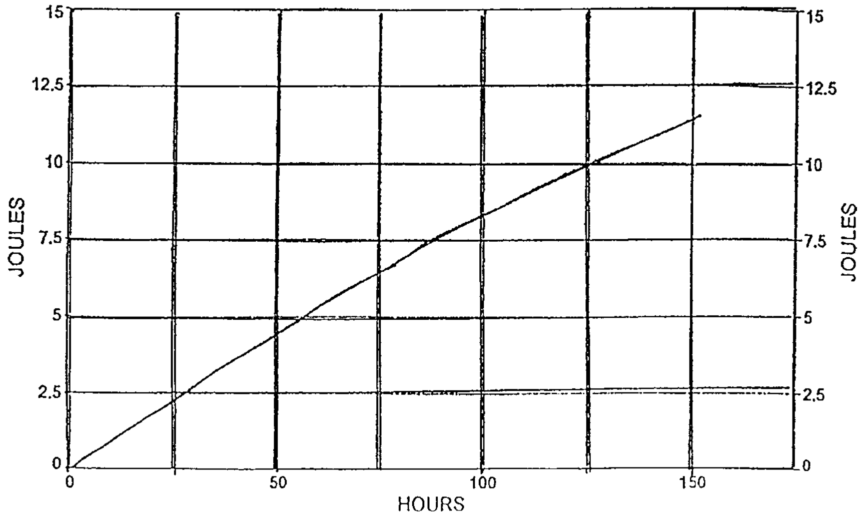

Fig. 7. IMC curve in joules of rerun HTPB propellant + sealants AB (1:1) at 70°C.

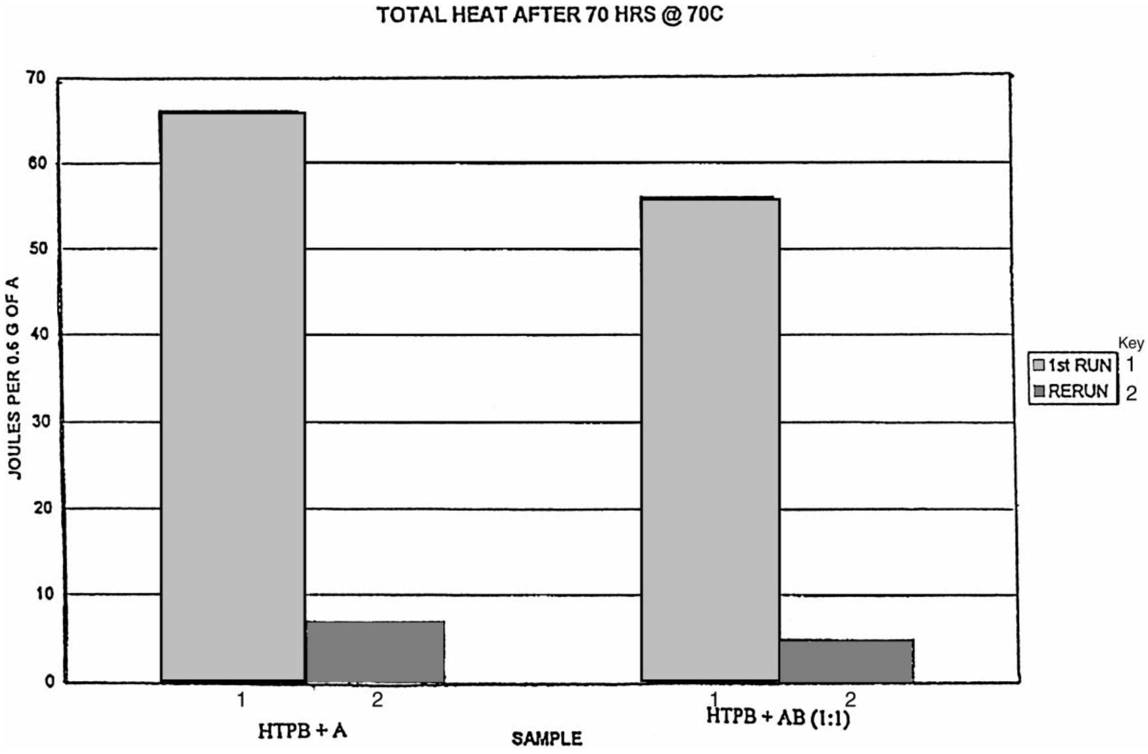

Fig. 8. IMC bar graph of initial and rerun of HTPB propellant and sealants A and AB (1:1) at 70°C.

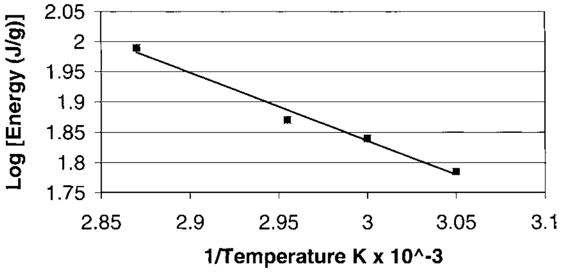

Fig. 9. IMC of HTPB propellant + sealant A.

reaction. This low value indicated that perhaps the diffusion reaction involved a free radical attack on the unsaturated linkage and an abstraction of the allylic hydrogen from the HTPB binder by the lead peroxide in sealant A. A DSC variable heating rate kinetic study was also carried out on this admixture. However, this was done in the decomposition region (>200°C) of the propellant. A decrease in the activation energy for the second peak (major peak, see Fig. 3) from 48 to 43 kcal/mol was found. This resulted in a 30-fold increase in the rate of reaction at 200°C in the admixture. DSC was not sensitive enough to measure the actual reaction between the ingredients in the admixtures.

3.3. *Cyclotrimethylenetrinitramine (RDX)+ ammonium benzoate (AB)*

Ammonium benzoate (AB) is the salt of a weak acid and a weak base. When heated it can liberate ammonia, which may react slowly with solid RDX to form nitrous acid and eventually destabilize RDX. RDX decomposes readily in the presence of strong bases (NaOH). The compatibility of RDX + AB was investigated by dynamic DSC and IMC. A DSC curve of AB in nitrogen in an uncrimped pan with an aligned cover showed the melting endotherm at 190°C that was in agreement with that reported in the Merck index. The melting endotherm is depended upon the sample confinement. In an open pan it was observed in 150°C region and in a sealed pan in the 210°C region. This variance is due to the liberation of ammonia gas when the sample melts. RDX decomposition curve at 2°C/min is shown in Fig. 10. It exhibits an HMX phase transition endotherm at 189°C followed by melt of RDX at 199°C immediately followed by exothermic decomposition with a major peak at 217°C. Admixtures of RDX + AB in molar ratios of 2:1, 1:1 and 1:2 were prepared. The curves were similar and had a peak maximum at 180 ± 0.5°C, and a typical curve is presented in Fig. 11 for 1:1 mixture in a sealed pan.

The large shift in peak temperature from 217°C for neat RDX to 180°C for RDX in the admixture was an indication of a large degree of incompatibility in this admixture in this temperature region. It may also be noted that the peak shape of the exothermic decomposition curve is much narrower in the admixture and also that it has a much higher rate of reaction at the peak maximum (15.8 versus 4.6 W/g). These are additional indications of incompatibility.

DSC kinetic analysis employing a variable heating rate method was carried out on RDX + AB admixture. A straight line plot was observed and the activation was calculated from the slope of the line. It was found to be 25.0 kcal/mol. Now the activation energy for RDX decomposition is well known and given as 47.1 kcal/mol [11]. This large shift in activation energies to a much lower value in the admixture indicated that a reaction occurred in the admixture and that it was incompatible in this temperature region (~150 to ~200°C).

Microcalorimetry data were obtained at 65.7, 70.7, and 76.8°C. The enthalpy values increased with time and temperature and the values after 100 h are presented in Table 3. An Arrhenius plot of the IMC data assuming a first-order reaction gave an activation energy of 33 kcal/mol. DSC kinetics gave a value of 25 kcal/mol. If the reaction mechanism were the same in the two experiments then similar activation energies would be expected with differences in frequency factors because of the differences in reaction temperatures in the experiments. However, there may be small differences in the reaction mechanism since in the DSC experiment the reaction is between a gas (NH_3) and solid/liquid RDX while in IMC it is

Table 3
IMC kinetic[a] after 100 h for RDX + ammonium benzoate (AB)

Temperature (°C)	65.7	70.7	76.8
J/g AB	5.0	14.2	24.3
Log J/g AB	0.70	1.05	1.39
10^3/K	2.952	2.910	2.859

[a] $E_a = 33\,\mathrm{kcal/mol}$ assuming a first-order reaction.

between a gas (NH_3) and solid RDX. The latter reaction would be expected to be much slower than the former and this is shown by the differences in activation energies with a larger value for the latter reaction. A rerun of the 70.7°C reaction after a delay of 4 weeks at room temperature resulted in an integral curve with a higher enthalpy of reaction which indicated that the reaction was continuing even at room temperature.

4. Conclusions

Compatibility determination of energetic materials in different temperature regions by DSC and IMC were in good agreement. Differences in the activation energies by DSC and IMC for the HTPB propellant and sealant A were due to different reactions being measured (i.e., free radical and decompositions). Differences in the activation energies for the reaction between an organic nitramine and an organic salt may be due to differences in the physical state of the nitramine, i.e., a liquid by high temperature DSC measurement and a solid by IMC in 65–77°C region.

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