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A THERMOCHEMICAL INVESTIGATION OF THE COMPLEX FORMED BY CYCLOTETRAMETHYLENETETRANITRAMINE (HMX) AND DIMETHYLFORMAMIDE (DMF)

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A THERMOCHEMICAL INVESTIGATION OF THE COMPLEX FORMED BY CYCLOTETRAMETHYLENETETRANITRAMINE(HMX) AND DIMETHYLFORMAMIDE(DMF)

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ABSTRACT

The heat of dissociation (ΔH_D) of the complex formed by cyclotetramethylenetetranitramine and dimethylformamide, HMX:DMF, was measured in DMF. ΔH_D for two reactions are reported: (a) $HMX{:}DMF(s) \xrightarrow{DMF(l)} \alpha\ HMX(s) + DMF(l)$, 5.2 kcal/mole is absorbed, (b) $HMX{:}DMF(s) \xrightarrow{DMF(l)} \beta\ HMX + DMF(l)$, 4.6 kcal/mole is absorbed. The difference in crystal energy between α HMX and β HMX as measured in acetone is 0.6 kcal/mole. A mechanism for the solution of HMX in DMF is proposed. The energies measured suggests that the bond forming the complex is due to van der Waals forces. It is also suggested that the dipole - dipole interaction makes a significant contribution to the bond energy.

CONCLUSIONS

1. The difference in crystal energy between α and β HMX is 0.6 kcal/mole.

2. The heat of dissociation of HMX:DMF to α HMX and DMF(1) is 5.2 kcal/mole. To form β HMX and DMF(1) 4.6 kcal/mole is absorbed.

3. The bond forming the complex is attributed to Van der Waals forces.

RECOMMENDATIONS

It is recommended that some of the experiments be repeated using a more uniform complex.

INTRODUCTION

HMX exists in four crystalline forms i.e. α, β, γ, δ. The β form is the most stable. When HMX is dissolved in DMF and recrystallized a one to one complex is formed i.e. HMX:DMF. Work in this laboratory shows that the HMX in the complex resembles the α configuration. The complex is quite stable at ambient temperatures and decomposes into the β form of HMX and DMF only after heating at 93°C Reference (8).

The nature of the bond (if any) forming the complex has to date defied identification. IR spectra and NMR studies have thus far been unsuccessful in elucidating the type of bond. In IR studies (for example) one sees a superimposition of the DMF spectra on the HMX spectra.

A thermochemical study was therefore undertaken to determine the energies involved in the reaction, between the two molecules, forming the complex, and if possible to determine the most probable classification of the bond based on the measured energies.

RESULTS

Table 1 shows the heat of combustion measurements made on the complex and on its constituents. All results are reported at constant volume and 25°C.

Table 2 lists the results of the dissociation measurements of the complex in DMF. Columns (3), (4), (5) and (6) shows the electrical calibrations parameters. Column (7) shows the corrected displacement of the potentiometer pen by the reaction. Column (8) is a list of the eight dissociation measurements in joules/gram. All determinations were made at 35°C to reduce the reaction time.

The heat of solution measurements were made at 25°C and are listed in Table 3. Column (1) lists the heat of solution of β HMX in DMF. Column (2) shows the heat of solution of β HMX in acetone, and Column (3) lists the heat of solution of α HMX in acetone. All values are endothermic. These measurements were made in the more sensitive calorimeter.

In Table 4 is listed the results of the immersion measurements of two different crystal sizes of HMX in DMF containing an excess of HMX. The column headings are the same as those in Table 2. Measurements are reported at 35°C.

Figure 1 is an example of a typical potentiometer record of a heat of dissociation measurement and an accompanying electrical calibration. The chart is 10 mv full scale, one inch in the vertical direction is equivalent to 8 minutes, and one graduation is equivalent to 1.7 joules. (approximate).

Figure 2 shows the temperature (in mv.) vs. time output when β HMX is dissolved in DMF. In the lower profile is shown a reaction conducted under slow stirring. The upper profile shows the output under rapid stirring.

Figure 3 shows the temperature vs. time profile for the solution of α and β HMX in DMF and β HMX in acetone. The recorder used has a full scale of 200 microvolts.

DISCUSSION OF RESULTS

ΔE_c Measurements:

Routine heat of combustion (ΔEc) measurements were made to determine the degree of additivity of the components in the complex. The heat of combustion of the complex reflects the sum of the heat energy of each of the two constituents as well as the energy binding these constituents. The heat liberated would not be additive if a high energy bond (ionic or homopolar) were present. Because small errors in combustion experiments may obscure the effect of a low energy bond, the combustion experiments can not be used to estimate the bond energy of the complex with confidence.

The results of the combustion experiments are listed in Table 1. For the complex the results obtained vary between 3024 cal/gram and 3120 cal/gram with an average value of 3067 ± 14 cal/gram. (14 cal/gram represents the standard deviation of the mean, i.e.

$$\sigma = \sqrt{\frac{\Sigma d^2}{n(n-1)}} \qquad \text{(Column (3).)}$$

If a one to one molar ratio is assumed for the complex, ΔE_c calculated from the combustion measurements made on DMF and HMX, (Columns (1), (2), Table 1) gives 3072 cal/gram. The calculated ΔE_c borders on the extremes of the combustion population for the complex. These experiments therefore confirm an approximate 1:1 combination of constituents and indicates a low energy bond.

The wide range in the combustion measurements of the complex greatly exceeds that which is ordinarily encountered in a "Parr" type adiabatic calorimeter. The usual heat of combustion measurement can be reproduced within a few tenths of one percent. This is evident in Columns (1), (2), Table 1. The poor reproducibility shows that the complex is not entirely homogeneous. Better reproducibility can probably be obtained if higher purity ingredients were used and the recrystallization process improved and controlled.

ΔH_D Measurements:

To obtain more quantitative information on the bond, the energy necessary to dissociate the complex (by solution in DMF) was measured. Approximately 1 gram of complex was dissolved in 300cc of DMF in a differential solution calorimeter. The results obtained are listed in Table 2 (A typical reaction showing the change in millivolt as a function of time is shown in Figure 1). A series of eight measurements were made accompanied by two to five calibrations per measurement. The heat absorbed in the dissociation is 5.2 ± kcal/mole. This energy is based on the following equation:

$$\text{(i) HMX:DMF(s)} \xrightarrow{\text{DMF(l)}} \text{HMX (solvated) + DMF(l)}$$

This equation applies however to a solvated HMX. To correct to α HMX(s) or β HMX(s) we must measure the heat of solution of solid HMX in DMF.

In making this series of measurements we note a very interesting phenomenon (Figure 2). The temperature vs. time profile shows that when the capsule containing β HMX is broken under DMF we get initially an exothermic reaction which becomes endothermic and finally reverts to zero (approximately). An example of two reactions are shown. In one experiment conducted with rapid stirring, the return to the initial temperature is faster than the one conducted with a slower stirring speed. This reaction shows that HMX with its great affinity for DMF may be forming the complex as it comes in contact with DMF. This complex dissociates however as the HMX becomes solvated. Because of the relatively long solution period however, the results were redetermined.

The new determinations were repeated in a smaller capacity calorimeter using high speed magnetic stirring. The smaller calorimeter has twice the sensitivity of the larger one i.e.(1.8 j/grad. vs. 0.9 j grad). Four runs were made. These are listed in Table 3, column (1). Under the new conditions we get a definite endothermic reaction. A temperature vs. time profile for two of the determinations is shown in Figures 3, (c) and 3 (d). The average endothermic heat of solution is 0.84 ± 0.03 kcal/mole. The disappearance of the initial exotherm in the solution process in these series of experiments is probably due to the use of smaller quantities of β HMX and the more efficient stirring.

In the solution of the α HMX in DMF, using the more sensitive calorimeter, we again get an initial exotherm followed by an endotherm with a zero change in enthalpy (Figure 3(a) and 3(b). The difference in the heat of solution between the two polymorphs gives a difference in crystal energy between α and β HMX of 0.84 kcal/mole.

Because of the complicated solution process in DMF the difference in crystal energy between the α and β polymorphs of HMX was redetermined in acetone. Here there are no complications. The reaction is strictly endothermic and takes place within a few minutes, Figure 3(e). The only assumption made is that the solvated HMX molecule is the same regardless of origin. The difference in the heat of solutinn between the two crystalline forms in acetone is approximately 0.6 kcal/mole, Table 3. This coroborates the differences obtained with DMF which is (0.8 kcal/mole). Because the acetone results are less complicated, 0.6 kcal/mole will be considered as the difference in lattice energy.

We can now write two equations; one for the dissociation of the complex to α HMX and the other to β HMX i.e.

$$\text{(ii)}\quad \text{HMX:DMF(s)} \xrightarrow{\text{DMF(l)}} \alpha\ \text{HMX(s)} + \text{DMF(l)}$$
$$- H = -5.2\ \text{kcal/mole}$$

$$\text{(iii)}\quad \text{HMX:DMF(s)} \xrightarrow{\text{DMF(l)}} \beta\ \text{HMX(s)} + \text{DMF(l)}$$
$$-H = -4.6\ \text{kcal/mole}$$

HMX when stored at room temperature will eventually change to the β form.

The difference in lattice energy confirms the greater stability of the β HMX. This can be shown by writing the acetone solution equations as follows:

$$\text{(iiii)}\quad \alpha\ \text{HMX} + \text{acetone} \longrightarrow \text{HMX solvated} \quad -H = -2.10\ \text{kcal/mole}$$

$$\text{(iiiii)}\quad \text{HMX (solvated)} \longrightarrow \beta\ \text{HMX} + \text{acetone} \quad -H = 2.68\ \text{kcal/mole}$$

$$\alpha\ \text{HMX} \longrightarrow \beta\ \text{HMX} \quad -H = 0.58\ \text{kcal/mole}$$

It is therefore seen that when α HMX changes to β HMX heat is evolved. Although there may be exceptions, the feasibility of a reaction can generally be determined by the direction of the change in enthalpy.

The greatest uncertainty in these measurements (excluding the experimental errors) is in all probability due to a water impurity in DMF. The affinity of DMF for water has been noted in these and other laboratories. The most probable role of the water in DMF is its adhesion to HMX. The heat of wetting of HMX in water was measured in this laboratory as a function of particle size of HMX, Reference 2. The results shows an exothermic reaction, the magnitude of which is dependent on the surface area of the particles.

This exothermic reaction may therefore compete with the endothermic dissociation measurements resulting in a reduction in the heat of dissociation. The error is considered marginal because in calculating the final dissociation energy a correction is included for the heat of solution of HMX in DMF. This cancels the effect of the solution of HMX formed in the dissociation of the complex.

Affinity of HMX for DMF:

The heat of solution experiments of HMX in DMF suggests the possibility that HMX reacts first with DMF to form the complex. If this is so we should expect the formation of the complex without resorting to complete solution and subsequent recrystallization.

Experiments were therefore conducted in which two β HMX samples, having different particles sizes, were immersed in DMF already containing an excess of HMX. The results obtained are listed in Table 4. The exothermic heats are substantial and independent of surface area. (This eliminates any possibility of a purely surface reaction). It was not possible to recover the HMX from the calorimeter without forming the complex.

Calorimetric conditions were simulated on the outside by stirring the added HMX for 15 minutes and separating the excess by filtration. The HMX was then dried in a vacuum oven at 50°C. Constant weight was attained after 15 hours. Heat of combustion measurements on the dried sample confirmed the 1:1 complex.

In another solution where the excess HMX was permitted to remain in contact with DMF overnight, only 8 hours of drying at 50°C was necessary to attain a constant weight. Combustion of the dried sample again showed a 1:1 complex. In each case the long drying period can be attributed to competiton between the formation of the complex and the evaporation of DMF. The result is the formation of the complex.

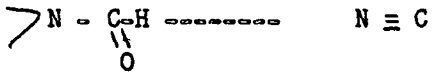
Type of Bonding

The magnitude of the dissociation energy (or interaction energy) suggests a molecular type compound. According to Ketelaar Reference (2) these compounds can be subdivided into three classes; inclusion compounds, electron-donor acceptor complex, and hydrogen bonded compounds. Although this classification may not be all inclusive it does account for the vast majority of molecular complexes reported to date i.e. those formed by van der Waals type bonds.

If one were to look for a hydrogen type bond in the complex, the aldehydic H in DMF would probably be the first to be investigated. Although DMF is known to H bond, it is always reported as the proton acceptor never the donor. Infra-red studies by Flett Reference 3 shows that DMF acts as the proton acceptor for phenol, diphenylamine and benzyl alcohol. There are cases however where aldehydes are shown to be the proton donors. Pinchas for examples Reference 4 suggests this type of bond in ortho-substituted benzaldehyde. Pimentel and McClellan suggest the possibility of H bonding by the aldehydic H atom in aldehydes Reference 5.

Because of this Castelli, Cragle, and Fredericks Reference 6 undertook an Infra-red study of HMX:DMF in which the aldehydic H atom in DMF is deuterated. A deuterated H atom is used because the numerous C-H groups in the complex mask the aldehydic H atom. The results obtained from this study show that there is no H bonding with the aldehydic A atom. These authors propose a resonances structure of DMF where the N atom carries a positive charge and the O atom is strongly negative.

In searching the literature for the dipole moment of DMF we came across a similar situation which confronted several Japanese investigators Reference 7. A mechanism was being sought for the solvent action of DMF on polyacrylonitrile. The conclusion reached is that there is no possibility of H bond formation by the aldehydic H in DMF i.e.



$$>N-\underset{\underset{O}{\|}}{C}-H\cdots\cdots\cdots N\equiv C$$

A structure similar to the one proposed by Castelli et al Reference 6 is reported. In addition to this it is reported that the aldehydic H atom in DMF has absolutely no ionic character.

Bedard, Huber, Myers and Wright have made a rather thorough study of the crystalline conformation of the HMX polymorphs. These authors suggest that the complex is not a clathrate, Reference 8. We are inclined to agree with these investigators, because dielectric measurements made on the complex and on its constituents (Reference 8) do not follow the trend shown for known clathrates as measured by Dryden and Meakin Reference 10. (This will be discussed in greater detail in the next section).

The reported electron-donor acceptor complexes which include nitro-compounds are those formed with benzene. The attraction in this type of complex is attributed to the bonding of the π electrons of the benzene ring with positive nitrogen atom of the nitro group, Andrews Reference 9. Although the complex in question does not fit this scheme, the possibility of an electron donor acceptor compound is not ruled out.

The results of a thermo-chemical study cannot be used to substantiate or disprove the point at which bonding occurs. The magnitude of the interaction energy does show however that the bond is formed by VanderWaals forces. Based on the work of Bedard et al Reference 8 and the dielectric properties of the compounds the authors suggest that a significant contribution to the bond energy is due to dipole-dipole interaction. The reasons are outlined in the subsequent section.

Dipole-Dipole Interaction:

The work at Canada (Reference 8) stimulates some interesting thoughts concerning the type of bonding forces involved in the complex. The proposed conformations of HMX are predicated on calculations of the atomic polarizations P_a. The P_a, values which they report are as follows:

β HMX = 5.3 cc
α HMX = 28.7 cc
γ HMX = 21.2 cc
HMX:DMF = 9.7 cc

The conformation proposed for α HMX which has the largest atomic polarization is that all of the aza nitrogens are in one plane and the methylene carbon atoms are in another. For the γ HMX (with the next highest atomic polarization) four methylene carbon atoms and two aza nitrogens are puckered out of a plane and the remaining aza nitrogens are above the plane. β HMX has all carbons in one plane with two aza nitrogens above and two below this plane.

Infra-red studies in this laboratory and in Reference 8 indicate however that the HMX in the complex is similar to the α HMX. If this is so then the atomic polarization of the complex should be closer to 20 cc and not 9.7 cc.

It is proposed that the low atomic polarization in the complex is due to the fixing of the highly polar nitramino groups by DMF. The response of these groups to an applied field is therefore substantially reduced.

It may be postulated that the reduction in the atomic polarization is due to spatial effects i.e. DMF occupies the empty spaces in the crystal lattics. Atomic polarizability however is responsive to the higher frequencies in the specturm (10^{12} cps). It is therefore doubtful whether this consideration is valid. Assuming however it is pertinent it can be shown that the effect of the DMF in the lattice is more than spatial in character.

Let us refer again to the work done in Canada, Reference 8. The following dielectric constants are listed:

β HMX = 3.087
α HMX = 4.671
γ HMX = 3.867
HMX:DMF = 3.180

It is evident that the dielectric constant (e) of the complex is significantly lower than that of the α or γ HMX. (It should be pointed out again that the HMX in the complex is similar to the α form and possibly the γ HMX but not the β HMX). Let us now compare this trend with the dielectric constants of known clathrates reported by Dryden and Meakin in Reference 10. These investigators determined the dielectric constants for quinol, the host compound, with and without various guest molecules. The following table is abstracted from their report:

Quinol compound	Dipole moment of polar molecule (ref. 3) (in D units)	8' at 50 kc/s	8' at 8,600 mg/s
Quinol cryst from alcohol		2.9	-
Quinol cryst from water		2.8	2.8
Clathrate compound with:			
Methanol	1.66	4.6	4.6
Hydrogen sulphide	1.1	3.4	3.2
Hydrogen cyanide	2.6 - 3.0	9.2	8.2
Methyl cyanide	3.4	3.1	3.1
Sulphur dioxide	1.7	3.9	3.7

It is noted that unlike the HMX:DMF complex the dielectric constant of each of the clathrates is greater than that of the quinol molecule. The smallest increase occurs in those clathrates where the guest molecules are largest thereby inhibiting orientation, methyl cyanide is an example.

Based on this it is proposed that the significant decrease in the dielectric constant of α HMX is due to interacting forces in the complex and not simple spatial effects.

The most obvious forces are those due to the high dipole moments of HMX, which is 4.68D (Reference 8), and DMF whose dipole moment is 3.82 (Reference 7). It is these forces which probably contribute significantly to the bond energy of the complex. It should also be noted that the dipole moment of DMF exceeds by far that value calculated from bond-moments, 2.73D.

Experimental Procedure:

All measurements were made in differential solution calorimeters. Two calorimeters were used. The results listed in Tables 2 and 4 were obtained in a calorimeter using 600 cc. Dewars, those in Table 3 were determined in 100 cc Dewars. In the larger capacity calorimeter a single motor drove twin stirrers, and the bath consisted of a system of three wooden boxes (air bath) regulated at 35 ± .01°C Figure 4. In the smaller calorimeter magnetic stirring was used and the calorimeter was submerged in a water bath at 25° ± .005°C. Each system was airtight.

To conduct an experiment the following procedure is used:

1. The Dewars are filled with solvent at the appropriate temperature.

2. The weighed sample bulb containing the dried sample is sealed and placed in position in the sample holder.

3. The top of the calorimeter, to which is sealed the stirrers, thermopile and sample holder, is fastened to the Dewars.

4. The calorimetric system is then permitted to condition in the bath overnight or until temperature equilibrium is attained.

5. Initial rating periods are obtained before the sample capsule is broken or before an electrical calibration. After equilibrium is reached a final rating period is taken.

6. Electrical calibrations are made before and after an experiment.

The electrical equipment used in each calorimeter assembly is as follows:

Equipment	Large Capacity Calorimeter	Small Capacity Calorimeter
Potentiometer	"White" Double Potentiometer Gray Instru. Company 1 μv graduations	Minneapolis Honeywell - Rubicon Instru. Model 2773 0.01 μv graduations
Power Supply	Bank of 6 volt batteries	Princeton Applied Research Power/Reference Model TC-602, Accuracy 0.1%
Timing	Manual Stop Watch 0.01 sec.	Hewlett-Packard Electronic Counter Model 522B 0.001 sec. Used automatically
Galvomometer System	Leeds & Northrup Model 2284A 0.39μv/mm-Moving Coil Reflecting	Sensitive Research Instru. Co. Photocell Galvonometer Amplifier Type 5214 with SR 21 Secondary Galvomometer Sensitivity used - 0.01μv/div
Recorder	Brown-Electronic 10 mv full scale Model Y 153-12	Leeds & Northrup Speedomax G 200μv full scale (special make)
Amplifier	Leeds & Northrup Model 9835B	None
Sensing Element	Thermopile 8 junction Iron-Constantan 36 Gauge	Thermopile 7 junction Iron-Constantan 36 Gauge

The calorimetric assembly, electrical circuit, and calibrations are adequately described in the literature References 11 and 12.

Samples

ΔEc and ΔH_D Experiments

1. **DMF** - Matheson, Coleman and Bell Inc. listed B.P. = 152-154°C, IR spectra showed no impurities.

*Index of Refraction 20°C = 1.4295 - 1.4295
Reference (13)= 1.4269

Probable Impurity - water

2. β **HMX** - Military grade - X-PA-PD-895, 3 May 1956 - IR spectra shows no impurities.

Melting Point 273.0 - 275.2

3. **HMX:DMF** - HMX(2) above was recrystallized from DMF(1) above.

Δ Hsoln Experiments

1. **DMF** - Matheson, Coleman and Bell Inc. listed B.P. = 152-154°C - Redistilled in laboratory - IR spectra shows no impurities

*Index of Refraction at 20°C = 1.4290 - 1.4280
Reference (13) = 1.4269

Probable Impurity - water

2. β **HMX** - Military Grade - Recrystallized three times from dry redistilled acetone. IR spectra shows no impurities.

Melting Point = 275.2 - 276.6

X-Ray Diffraction shows only form.

3. **α HMX** - Recrystallized β HMX (above) from 70% HNO_3.

X-Ray Diffraction shows only α form.

Melting Point = 275.2 - 276.6

4. <u>Acetone</u> - Redistilled three times from reagent grade acetone and kept over $CaCl_2$.

*Index of Refraction = 1.3580 - 1.3582
Reference (14) = 1.35886

*Index of Refractions and Melting Points determined by Instrumental Analysis Research Unit, Report No. 63-VGl-38 - Nov 1963.

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TABLE I

Heat of Combustion Measurements at 25°C and Constant Volume, Cal/Gram*

(1) β HMX	(2) DMF	(3) HMX:DMF** Batch A
2303.8	6228.6	3037
2303.0	6222.2	3050
	6229.8	3024
		3086
		3120
		3082
2303.4	6226.8	3067

$$\sigma = \sqrt{\frac{\Sigma d^2}{(n-1)}} = \pm 36$$

$$\sigma = \sqrt{\frac{\Sigma d^2}{(n-1)n}} = \pm 14$$

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*Heat of Combustion measurements are reported by Mr. G. Silvestro, Propellant Research Section Report No. 60-VE4-191, 10 June 1960.

**Used in Immersion Experiments.

TABLE 2

Heat of Dissociation of HMX:DMF at 35°C

(I) Sample	(2) Weight (gram)	(3) Volts	(4) Amps	(5) Time (Seconds)	(6) Calibration Constant Joules/graduation	(7) △ H_D Output (graduations)	(8) △ H_D Joules/gram
A	1.0027	3.240324 3.240324	0.19966 0.19966	83.52 104.63	1.698 1.670 1.684	38.71	-65.01
	0.9655	3.210321 3.220322	0.19978 0.19988	91.13 91.28	1.733 1.777 1.755	37.48	-68.12
B	0.9800	3.357354 3.355352 3.356353 3.354351	.2064646 .2063648 .2063647 .2061649	161.42 66.32 68.93 144.63	1.633 1.675 1.660 1.674 1.668	35.10	-59.74
	0.8386	3.311308 3.312309 3.308305 3.326323	.2054692 .2055691 .2053695 .2065677	61.16 104.17 104.46 98.32	1.628 1.676 1.701 1.667 1.668	32.8	-65.24
C	0.7996	3.310316 3.322319 3.317314 3.306303	.2050684 .2060681 .2057686 .2047697	105.51 136.02 126.88 183.70	1.672 1.701 1.686 1.703 1.690	28.5	-60.24
	0.9784	3.326323 3.338335 3.344341 3.342339 3.326323	.2047677 .2054665 .2057659 .2057661 .2046677	96.72 103.38 68.78 123.92 106.12	1.665 1.661 1.657 1.674 1.674 1.662	27.4	-46.56
D	0.7557	3.268265 3.262259 3.249246 3.270267	.2028735 .2025741 .2016754 .2021733	83.43 72.27 98.88 69.72	1.4740 1.477 1.470 1.477 1.477	38.8	-58.62
	0.9984	3.290287 3.277274 3.271268	.2023713 .2915726 .2011732	69.26 111.01 87.00	1.571 1.605 1.605 1.594	32.7	-52.20

TABLE 3

Heat of Solution of β and α HMX at 25°C

(1) $-\Delta H_{soln}$ β HMX in DMF j/g		(2) $-\Delta H_{soln}$ β HMX in Acetone j/g	(3) $-\Delta H_{soln}$ α HMX in Acetone j/g
-11.15			
-12.86		-36.90	-28.08
-12.23		-35.76	-30.43
-12.09		-40.75	-30.34
-11.83	Average	-37.80	-29.62
-0.84 ± 0.03 kcal/mole		-2.68 ± 0.10 kcal/mole	-2.10 ± 0.05 kcal/mole

TABLE 4

Heat of Wetting of HMX in DMF Saturated with HMX

(1) Sample	(2) Weight (gram)	(3) Volts	(4) Amps	(5) Time (Seconds)	(6) Calibration Constant Joules/graduation	(7) $\triangle$H output (graduations)	(8) $\triangle$H Joules/gram
Fine	1.0631	2.261259	0.1406241	128.42	1.848		
		2.262260	0.140774	100.61	1.831		
					1.840	25.2	43.616
Fine	1.0319	2.246244	0.1397756	121.882	1.849		
		2.245243	0.1396757	197.021	1.867		
					1.858	16.9	30.43
Fine	0.7728	2.281279	0.1394721	104.297	1.929		
		2.290288	0.1392772	107.590	1.928		
					1.929	12.3	30.69
Coarse	1.6557	2.2447425	0.13917575	193.706	1.874		
		2.247245	0.1394755	181.141	1.862		
		2.244242	0.1392758	181.238	1.876		
		2.2487465	0.13957535	183.969	1.869		
		2.244242	0.1395758	267.471	1.874		
					1.871	39.3	44.41
Coarse	1.0042	2.289287	0.1397713	121.091	1.967		
		2.287285	0.1396715	101.491	1.942		
					1.955	22.1	43.025
Coarse	1.0033	2.246244	0.1397756	180.31	1.834		
		2.242240	0.139476	180.45	1.826		
					1.830	33.1	60.440

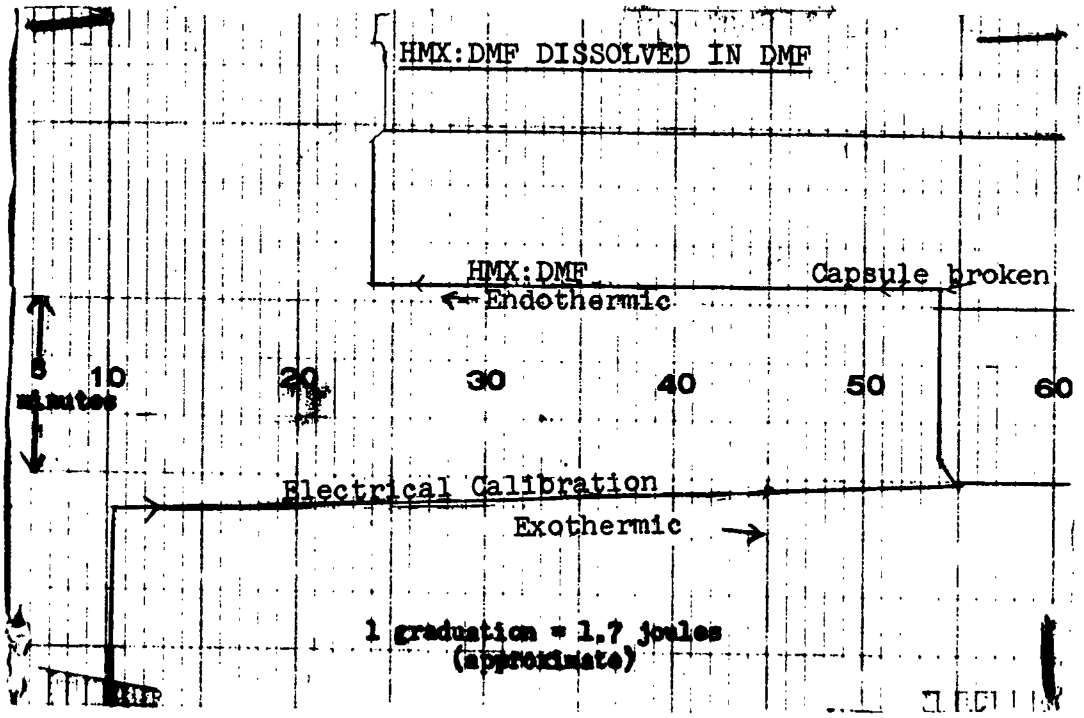

HMX:DMF DISSOLVED IN DMF
HMX:DMF
← Endothermic
Capsule broken
5 minutes
10
20
30
40
50
60
Electrical Calibration
Exothermic →
1 graduation = 1.7 joules
(approximate)

Figure 1

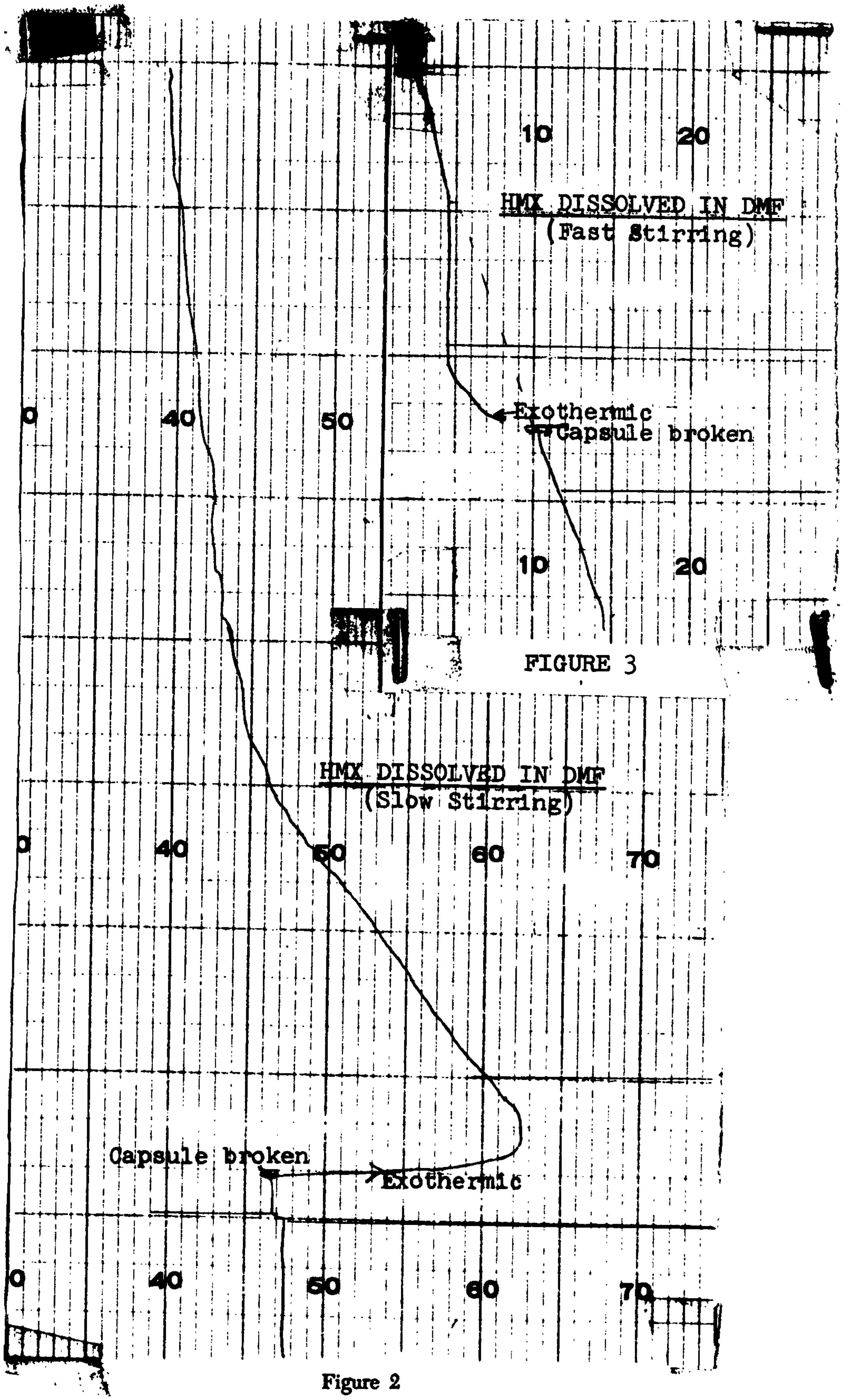
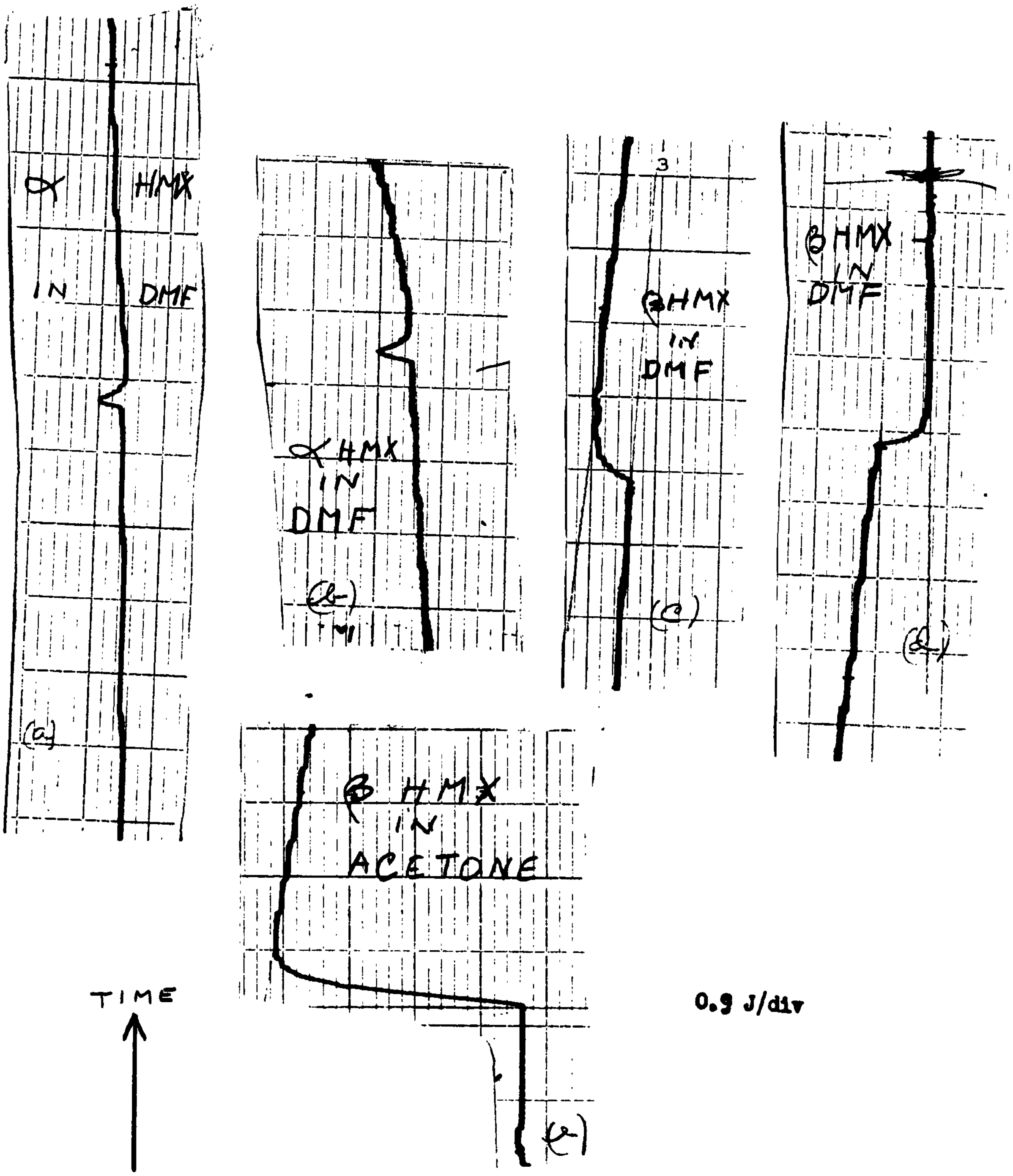


FIGURE 3

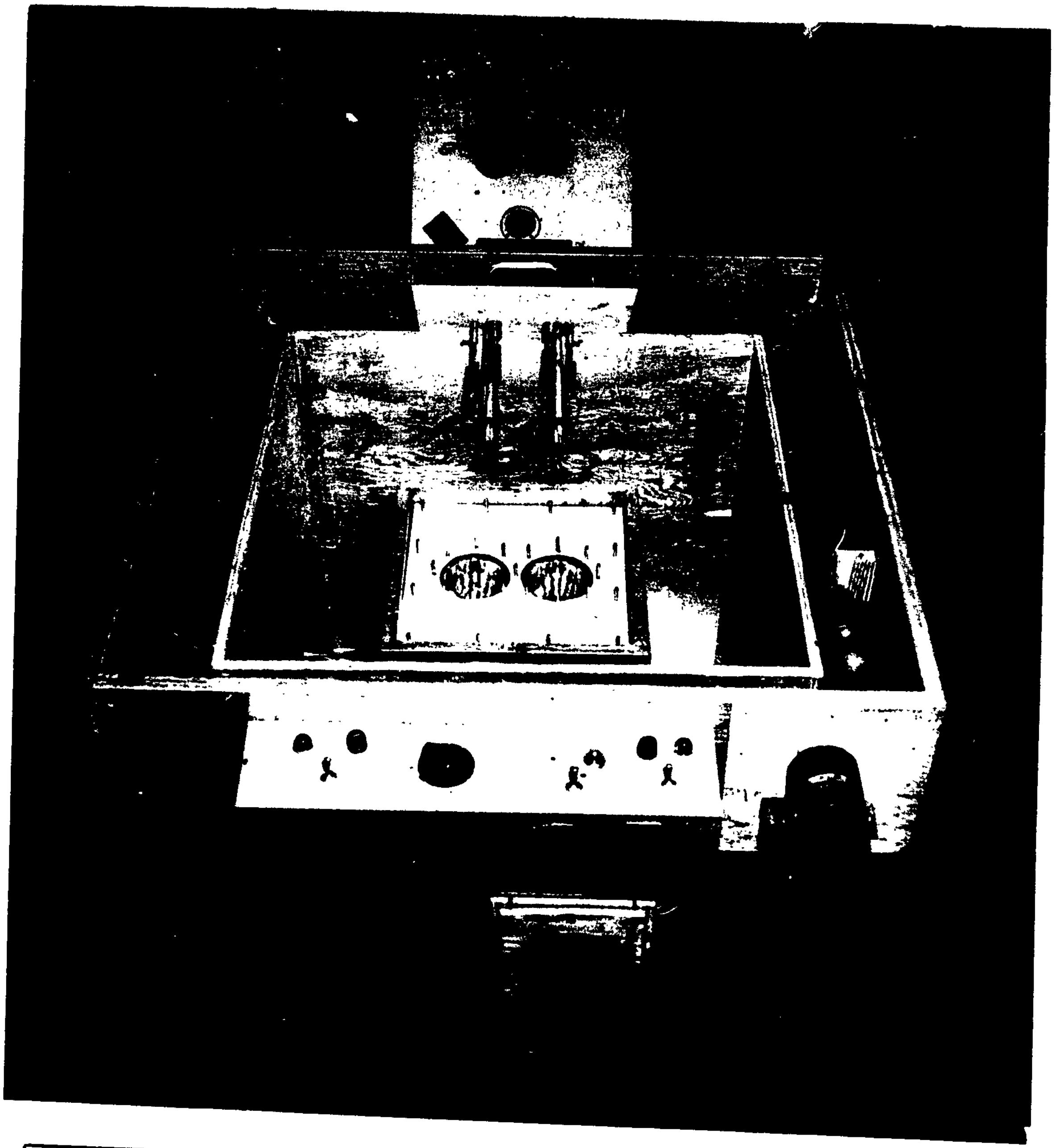
Figure 2



0.9 J/div

Temp. vs. Time Profiles

Figure 3



28-017-230/Ord-62 **PICATINNY ARSENAL** **ORDNANCE CORPS**

Figure 4 Differential Calorimeter Assembly

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A THERMOCHEMICAL INVESTIGATION OF THE COMPLEX FORMED BY CYCLOTETRAMETHYLENETETRANITRAMINE (HMX) AND DIMETHYLFORMAMIDE (DMF)

Charles Lenchitz, Rodolph Velicky

Tech. Memorandum No. 1343, DA Project 1A222901A211 February 1964, 19 pp., tables and figures.

The heat of dissociation (ΔH_D) of the complex formed by cyclotetramethylenetetranitramine and dimethylformamide, HMX:DMF, was measured in DMF. ΔH_D for two reactions are reported:

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2. Dimethylformamide — Dissociation

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