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A STUDY OF PROPELLANT DECOMPOSITION BY DIFFERENTIAL SCANNING CALORIMETRY

J. E. HOUSE, Jr., CHARLES FLENTGE AND PAUL J. ZACK
Department of Chemistry, Illinois State University, Normal, IL 61761 (U.S.A.)
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ABSTRACT

The decomposition of 12 commercial nitrocellulose propellants was studied by differential scanning calorimetry. In general, heats of decomposition were found to be about 400–475 cal g^{-1} for all the propellants when the reaction produced 12–16% residue. Some samples decompose in a much different way, producing only about 3–4% residue and liberating only 200–250 cal g^{-1}. Both decomposition patterns were observed for samples of the same propellant run in the same way. In almost all cases, different manufacturing lots of the same propellant do not appear to show a significant difference in heat content. It appears that neither reprecipitation nor prolonged drying materially affects the heat of decomposition of the propellants.

INTRODUCTION

Propellant powders for use in small arms are predominantly nitrocellulose, although some powders contain 10–15% of nitroglycerin added. Single-base propellants are those containing only nitrocellulose while double-base powders are those containing both nitrocellulose and nitroglycerin. The identification of these materials is of considerable importance to forensic scientists. One of the promising techniques for identifying specific propellants is thermal analysis.

Calorimetric studies on propellants are usually carried out under high pressure conditions to simulate actual conditions of use. This procedure is not practical as the basis for a routine test. Recently, however, DeHaan has reported heats of decomposition determined by DTA for several propellants of the types used in small arms ammunition[1]. Unfortunately, a given propellant was reported to have a great range of heat of decomposition.

Our recent DSC study of a small number of propellants has shown that the heat of decomposition is uniform for a given propellant[2]. A complicating feature here is that the heat of decomposition released at atmospheric pressure is considerably different than the heat of decomposition released at a pressure of several hundred atmospheres. Our initial investigation did show that although most samples of a given propellant gave the same heat of decomposition, an occasional sample would behave differently and give a much lower value.

In the present study, a large number of propellants have been studied using DSC. In some instances, propellants can be separated from other materials by an extraction process. Studies have also been conducted on some propellants which have been dissolved and reprecipitated to see how this process affects the heat of decomposition. Finally, we have conducted studies on propellants which have been stored at elevated temperatures to determine the effects on thermal decomposition.

EXPERIMENTAL

DSC studies were carried out as reported previously[2, 3]. Heats of decomposition were obtained by integration of peak areas and comparing to a standard using the fusion of metallic tin. Residue weights were determined by cooling the sample pan to room temperature and reweighing.

Propellants used in this study were commercially available cannister materials used in small arms applications. Materials used included those having individual particles in the forms of cylindrical rods, short cylinders with axial holes, discs, and spheres. Experience has shown that while the physical attributes of the propellant have a great bearing on its properties under conditions of use, they have no measurable effect on its heat of decomposition.

Thermal effects produced by normal drying procedures were determined by heating propellants of various types in an oven at 100°C and removing samples as desired. Reprecipitated propellants were obtained by dissolving the desired propellant in acetone, filtering, and removing the acetone under vacuum. The propellants so treated were obtained as nitrocellulose films on the walls of the container. Discs of these films were used in DSC studies.

RESULTS AND DISCUSSION

A single exothermic peak beginning around 185–190°C is observed in the DSC curves for the propellants. Generally, these have about the same profile for most of the propellants. In some cases, however, the same propellant gave two different types of curves, even for consecutive samples run in exactly the same way. It was found that the heat released was greatly different in these instances. This behavior suggested that the decomposition does not proceed in the same way with every sample of a given propellant.

In order to clarify this situation, the amount of solid residue remaining after the decomposition is complete was determined. On this basis, it is established that two different reaction types are observed. The first is:

Propellant → volatile products + 12–16% residue (1)

and the second is:

Propellant → volatile products + 2–5% residue (2)

Reaction (1) involves no ignition and has the higher ΔH value. Reaction (2) involves

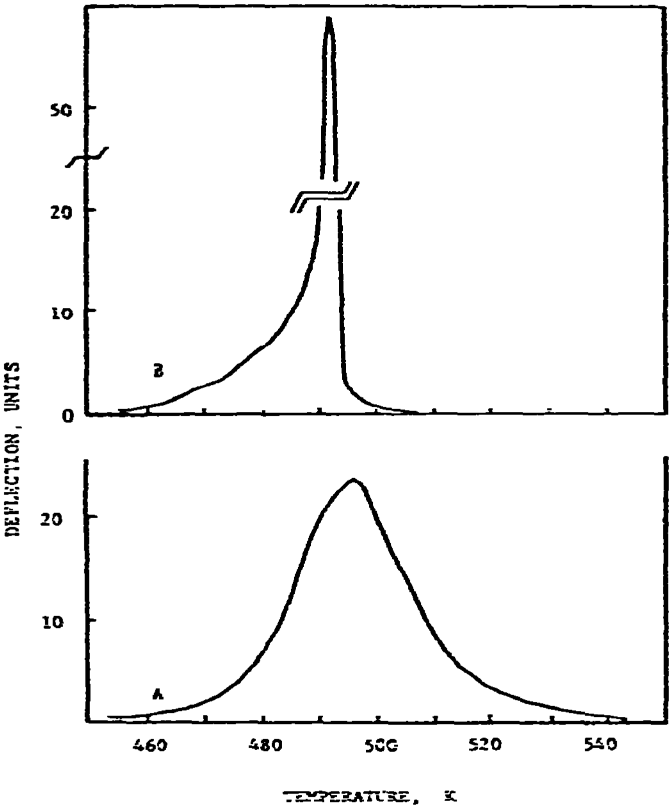

Fig. 1. DSC curves for the decomposition of samples of DuPont 700X propellant. Curve A is for a 1.16 mg sample decomposing according to eqn (1) and yielding a ΔH of —506 cal g^{-1}. Curve B is for a 1.13 mg sample decomposing according to eqn (2) and yielding a ΔH of —300 cal g^{-1}.

ignition and frequently resulted in sample pans and lids being blown apart. Previously, it had been found that one sample out of perhaps 15 gave an unusually low heat of decomposition[2]. It now appears that, for some propellants, the decomposition takes place by eqns (1) and (2) with about equal frequency. Figure 1 shows typical DSC curves obtained for these two types of behavior. Although some of the propellants used in this study were found to exhibit both types of behavior, some gave only one type or the other, but not both.

The heats of decomposition found for the various propellants are shown in Table 1.

The results indicate that there is no significant difference between the heats of decomposition of the propellants as long as eqn (1) is followed. Although as many as ten samples of a propellant were run in some cases, the ΔH values are within experimental error for almost all the propellants used. It appears to make no difference whether the propellant is single or double base. Some of the propellants have individual particles which are of greatly differing shapes, although this seems to have little effect on the heat of decomposition as measured here. This difference does, however, produce a great difference under conditions of use.

TABLE 1

THERMAL PARAMETERS FOR DECOMPOSITION OF UNTREATED PROPELLANTS

Propellant	*Source*	*Type*	*Reaction*[a]	$-\Delta H(\mathrm{cal\ g^{-1}})$[b]	*% Residue*[b]
473 AA[a]	Olin	DB	(1)	440 ± 19	11.9 ± 1.7
473 AA[a]	Olin	DB	(2)	227	3.3 ± 0.5
IMR-4320[a]	DuPont	SB	(1)	459 ± 33	12.4
IMR-4320[a]	DuPont	SB	(2)	182 ± 11	1.7 ± 0.8
IMR-3031[a]	DuPont	SB	(1)	428 ± 11	—
IMR-3031[a]	DuPont	SB	(2)	189 ± 12	3.8 ± 0.8
Red Dot[a]	Hercules	DB	(1)	455 ± 25	16.5 ± 2.5
Red Dot[a]	Hercules	DB	(2)	224 ± 30	2.4 ± 2.0
700X[a]	DuPont	DB	(1)	518 ± 12	12.1 ± 0.9
700X[a]	DuPont	DB	(2)	274 ± 24	1.4 ± 0.9
Green Dot[a]	Hercules	DB	(1)	484 ± 26	13.4 ± 1.4
IMR-4895[a]	DuPont	SB	(1)	416 ± 15	16.2 ± 2.8
IMR-4895[a]	DuPont	SB	(2)	179 ± 9	4.6 ± 0.9
Bullseye[a]	Hercules	DB	(1)	325 ± 8	11.0 ± 1.1
IMR-4198[a]	DuPont	SB	(1)	438 ± 26	18.5
2400[a]	Hercules	DB	(1)	405 ± 31	—
Unique[a]	Hercules	DB	(1)	448 ± 10	—
IMR-4227[a]	DuPont	SB	(i)	453 ± 40	—

[a] Reaction (1): no ignition with 12–16% residue; reaction (2): ignition, low apparent ΔH, and 2–5% residue.

[b] Mean values ± average deviation from the mean.

It would normally be expected that the more complete the decomposition (lower the amount of residue), the greater would be the amount of heat liberated. However, the data shown in Table 1 indicate that the opposite effect is seen. In cases where ignition occurred, the reaction of Type B produced an apparent ΔH of only about half that obtained when the same powder decomposed by a Type A reaction. It is likely that the ΔH is not accurately measured in such rapid decomposition.

Aside from the low ΔH values found during the fast reactions, there was a significant difference in the amount of residue. A major problem in utilizing thermal decomposition of propellants in analysis is that samples of the same propellant studied under identical conditions can result in different values for ΔH. In fact, most of the powders studied showed this behavior, even though all runs were carried out under identical conditions. Previous workers have failed to recognize that only two ΔH values are obtained and have reported a range of values[1]. However, this work has shown that a given propellant yields one of two ΔH values and the values obtained are usually reproducible to within a few percent.

Batch effects

Although propellant manufacturing processes produce uniform materials, it was felt that differences might exist for different manufacturing lots. Table 2 shows heats of decomposition for selected propellants.

TABLE 2

HEAT OF DECOMPOSITION OF DIFFERENT LOTS OF PROPELLANTS

Propellant	*Lot No.*	$-\Delta H$ (cal g^{-1})	
		Mean	± *Average Deviation*[a]
Hercules 2400[a]	339	405	31
Hercules 2400[a]	381	400	14
Hercules Unique[a]	519	458	14
Hercules Unique[a]	526	438	12
Hercules Unique[a]	UN026	447	4

[a] Average deviation for 10 samples of each.

The data in Table 2 show that the values obtained for the heat of decomposition do not vary greatly. In fact, the values for the two lots of Hercules 2400[a] are almost identical. However, the variation in heat of decomposition of Hercules Unique[a] differed more by manufacturing lot. Three different lots of this propellant were examined and the *t*-test used to determine if a significant difference exists. The *t*-test coefficients show that the difference between Lots 519 and 526 (average heats of decomposition of 458 and 438 cal g^{-1}, respectively) is significant at the 95% confidence level. However, the difference between Lot UNO26 (heat of decomposition of 447 cal g^{-1}) and the other two lots is not significant. Therefore, there is a statistical difference between lots of Hercules Unique[a] having the lowest and highest ΔH values, but not between lots having a smaller difference in ΔH values. It is unlikely that differences in thermal characteristics of manufacturing lots are large enough to be significant in most cases.

Decomposition of reprecipitated propellants

In order to determine if a propellant can be separated from other materials by extraction and still behave normally, four propellants were selected for reprecipitation studies. For these cases, the thermal data are shown in Table 3. Both single-base and double-base propellants were selected in order to see if the nitroglycerin present in double-base propellants caused them to behave differently upon reprecipitation.

TABLE 3

HEATS OF DECOMPOSITION OF REPRECIPITATED PROPELLANTS

Propellant	*Type*	$-\Delta H$ (cal g^{-1})	
		Mean	± *Average deviation*
DuPont IMR-4198[a]	Single base	523	37
DuPont IMR-4227[a]	Single base	512	15
Hercules 2400[a]	Double base	441	24
Hodgdon BL C-2[a]	Double base	445	5

TABLE 4

HEATS OF DECOMPOSITION OF PROPELLANTS DRIED FOR VARIOUS LENGTHS OF TIME AT 100°C

Propellant	$-\Delta H$ (*cal g*$^{-1}$ *for heated samples*)				
	2 h	*3 h*	*8 h*	*7 days*	*1 mo.*
DuPont IMR-4198[a]	403	431	435	347	382
DuPont IMR-4227[a]	414	403	372	391	393
Hercules 2400[a]	358	321	364	467	407
Hercules Unique[a]	440	422	400	486	509

The heats of decomposition shown in Table 3 can be compared to those in Tables 1 and 2 and those previously reported[2]. In each case, it is readily apparent that the heat released is within experimental error of that amount released by the untreated propellant. Therefore, it should be possible to separate a propellant by acetone extraction and still quantitatively determine the propellant by thermal decomposition.

Dried propellants

In order to determine the effect of removing last traces of volatile solvents from propellants on their heats of decomposition, several propellants were maintained at 100°C. Samples were removed after various lengths of time and DSC runs carried out in the usual way. The results of these runs are shown in Table 4.

The data in Table 4 do not show a definite trend. It is not apparent exactly how heating a sample for several hours or days affects the heat of decomposition since the values are, for the most part, within experimental error. It is obvious, however, that drying evidential materials at reasonable temperatures would not interfere with subsequent thermal analysis for propellants in the samples.

CONCLUSION

As previously reported[2], the decomposition of nitrocellulose propellants does not produce a wide range of ΔH values[1]. It does, however, involve more than one process in an apparently random way for some propellants. Extensive drying of propellants and reprecipitation after extraction do not significantly alter the heat of decomposition. Batch effects appear to be slight. These data and observations provide a basis for analyzing evidential materials in forensic applications and a framework for interpreting the results.

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