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THERMAL DECOMPOSITION STUDIES ON DOUBLE-BASE PROPELLANT COMPOSITIONS

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Thermal reactivity studies were carried out in the temperature range 100–160° on two double-base propellant compositions which differ significantly in chemical composition, calorimetric value and ballistic characteristics. The course of decomposition was followed by two methods: (i) determining the rate of NO evolved with the Bergman and Junk method; (ii) estimating the volume of gases evolved in a vacuum stability test method. The activation energy values computed using the Arrhenius equation and the Jacobs–Kureishy method were comparable and in the range 134–170 kJ mol^{-1}. In the temperature range 100–140°, nitroglycerine volatilization was significant during the early stages of heating. Above 180°, the rate of decomposition was very fast, leading to ignition of the propellant, followed by slow oxidation of the carbonaceous residues. The thermoanalytical data indicated a two-step decomposition process for propellant I, and a single-step process for propellant II.

Propellants must often be stored for long periods under adverse environmental conditions. The nitroester components of double-base (DB) propellants, i.e. nitrocellulose (NC) and nitroglycerine (NG), are susceptible to saponification with time, and they continue to decompose even in the presence of added stabilisers; the rate depending upon temperature, humidity and other conditions of storage. Since the ballistic performance of propellants is dependent upon their physico-chemical conditions at the time of use, a knowledge of their thermal decomposition characteristics is of interest from the points of view of assessing their useful shelf life and of gaining an insight into the nature of the reactions taking place. This paper discusses the results of thermal reactivity studies on two DB propellant compositions which differ significantly in chemical composition, calorimetric value and ballistic properties. The reactivities were studied by the following methods: determination of the rate of evolution of NO with the Bergman and Junk (B & J) method, estimation of the rate of evolution of non-condensable gases using a vacuum stability test (VST) apparatus, differential

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thermal analysis (DTA) and thermogravimetry (TG). Ignition delay times (D_t) in the temperature range 180–220° were also investigated.

Experimental

The percentage compositions and calorimetric values of the DB propellants studied are given in Table 1. A solid sample or propellant I was carefully ground and sieved between US standard sieves nos 10 and 20, and the fraction retained on sieve 20 was used for the experiments. Propellant II was in the form of thin square flakes with a thickness of 0.1 mm and side dimensions of 1.0 mm. Samples were dried at 50° for 1 hour prior to use.

Table 1 Percentage compositions, calorimetric values and ignition temperatures of propellants I and II

Ingredients	Propellant I, %	Propellant II, %
Nitrocellulose	57.5 (12.3% N_2)	58.3 (12.8% N_2)
Nitroglycerine	26.2	39.5
Ethylcentralite	–	1.7
2-Nitrodiphenylamine (NDPA)	1.4	–
DNT + TNT	6.1	–
Dibutylphthalate (DBP)	5.0	–
Additives	–	0.5
Inorganic salts	3.8	–
Calorimetric value (J g^{-1})	3583	5082
Ignition temperature, °C *	180	175

* determined at a heating rate of 5 deg min^{-1} on 100 mg samples.

The B & J method followed was similar to that described in the literature [1], except that 100 mg samples were taken for experiments in order to minimize the self-heating effect and to avoid the risk of explosion associated with the heating of a large quantity of sample at high temperatures. 100 mg samples were taken in several B & J test tubes, which were then subjected to isothermal heating in an electrically heated metal block provided with 24 heating holes and temperature control within ±0.5 degree. At fixed time intervals a tube was removed from the bath and the liberated NO was estimated by titrimetry [1a]. The procedure was continued until the volume of NO evolved showed no appreciable increase with further duration of heating. Decomposition was carried out at 100, 110, 120, 130, 140 and 160°.

The VST was carried out in the same manner as described in the literature [1b], except that 50 mg samples were used for tests. Electrically heated glycerine + water mixture baths adjusted for temperature 120, 130, 140 and 150° were used to heat samples. The volume of gases evolved at fixed intervals of time was calculated for satndard conditions from the observed pressure increase in the capillary.

Ignition temperatures and ignition delay times (D_t) were measured using a Julius Peter explosion temperature bath provided with automatic temperature rise at 5 deg min^{-1}. The effect of sample mass on the ignition delay time was measured at a fixed temperature of 190° on a sample mass in the range 20–120 mg.

TG, DTG and DTA curves were recorded simultaneously on a Netzch SA 409 thermoanalyzer, in both air and dynamic N_2 atmospheres, at a heating rate of 10 deg min^{-1}. IR spectra of the condensates were recorded as films between NaCl windows with a Perkin–Elmer 683 IR spectrophotometer.

Results

Bergman and Junk method

The volumes of NO liberated in the B & J method for propellants I and II at various temperatures are given in Table 2. The higher NO volume obtained for propellant II as compared to propellant I at all temperatures is in conformity with the higher nitrogen content of the NC, and the higher NG content in the composition. Appreciable NG volatilization was observed in the early stages of heating; this condensed on the cooler sides of the B & J tube. Experiments were conducted with 2.0 g samples of propellant II to determine the NC and NG contents of the residues after heating at 120° for various periods. The results are shown in Table 3. The NG lost was recovered almost quantitatively by extracting with ether the condensates on the cooler sides of the B & J tube. It may be seen from Table 3 that the rate of NG loss is significant (3–4%) during the first 2 to 4 hours of heating, whereas the loss in NC is comparatively small during this period, but becomes significant at later stages. Thus, NG volatilization from the surface of the propellant appears to be the major process occurring during the early period of heating at lower temperatures.

Table 2 Volumes of NO and total gases evolved from propellants I and II in B & J and VST method, respectively, at various temperatures at the end of the acceleratory phase

Temp., °C	Duration of decomposition, hours	Propellant I B & J NO, ml	Propellant I VST Total gases, ml,	Propellant I Ratio	Propellant II B & J NO, ml	Propellant II VST Total gases, ml	Propellant II Ratio
120	170	4.0	4.4	1.1	5.6	6.8	1.2
130	120	6.3	7.5	1.2	7.6	11.4	1.8
140	70	6.5	10.4	1.6	7.8	20.5	2.6
150	15	6.8	14.8	2.2	8.0	32.0	4.0

Table 3 Chemical analysis of propellant II residues after heating at 120° for various periods

Ingredient	Initial percentage	Percentage composition after heating		
		2 hours	6 hours	22 hours
Nitrocellulose	58.3	58.1	57.3	47.6
Nitroglycerine	39.5	37.2	36.4	35.0
Ethylcentralite	1.7	1.2	1.0	0.98

The volume of NO versus time curves were sigmoid in shape and the data fit a first-order rate equation. In the temperature range 120–160° the activation energy values derived from the Arrhenius relationship were 136.9 kJ mol^{-1} and 149.5 kJ mol^{-1}, respectively, for propellant I and propellant II. The B & J test on propellant II in the low-temperature range 100–130° gave an E value of 311 kJ mol^{-1}.

Vacuum stability test (VST) method

Isothermal decompositions in the VST method were carried out under an initial vacuum of approximately 730 Torr of air. Typical curves of volume of evolved gases versus time for propellant II are shown in Fig. 1. At 120°, where the decomposition was slow, an extended scale of the volume versus time curve showed four distinct regions: a long induction period, preceding a slow decomposition stage extending up to about 110 hours, followed by an acceleratory phase up to about 220 hours, which then gradually slows down. The induction period rapidly decreases above 140° and the acceleratory phase is followed by a gradual deceleratory phase; this takes several hours to attain a steady state, depending upon the temperature. The activation energy values

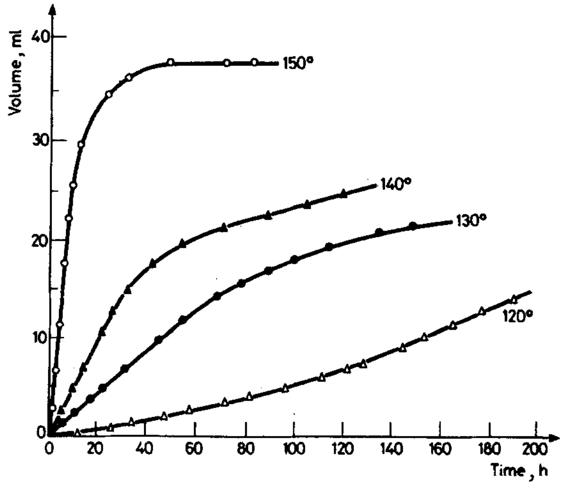

Fig. 1 Typical curves of volume of evolved gases vs. time for propellant II from VST method

calculated using the Arrhenius relationship for the phase ending with the acceleratory period were 137 kJ mol^{-1} and 170.5 kJ mol^{-1}, respectively, for propellants I and II.

Methyl violet tests on residues left after the acceleratory period were negative, indicating the complete dissociation of ON bonds during the acceleratory phase. The volume of total gases evolved at various temperatures towards the end of the acceleratory phase, and the ratio of total gases to volume of NO liberated in the B & J method at the respective temperatures, are also included in Table 2. Below 130°, the ratios remain approximately constant in both cases, but they increase rapidly with increase in temperature. This would imply that ON bond dissociation is the predominant reaction occurring at lower temperatures, and at higher temperatures the reaction proceeds further, involving oxidation of the organic moities and resulting in the formation of additional gases.

Droplets of yellow and colourless condensates, respectively, were observed on the cooler sides of the VST tubes in the cases of propellants I and II. For recording of the IR spectra of the condensates, 250 mg of each propellant was heated in a wide-mouthed VST tube at 130° for 0.5 hours. The spectra of the condensates, recorded as films on NaCl windows (Fig. 2), exhibit dominant absorptions characteristic of NG in the following regions (cm^{-1}): 2980 ν(C–H), 1745 $\nu_{as}(NO_2)$, 1280 $\nu_s(NO_2)$, 1015 ν(C–O), 840 $\delta(NO_2)$ and 755 ν(O–N). Additional weak absorptions present in the spectrum of the yellow condensate from propellant I in the frequency regions (cm^{-1}) 3300 ν(N–H), 1740 ν(CO), 1545 $\nu_{as}(C–NO_2)$ and 1360 $\nu_s(C–NO_2)$ are attributable to the presence of 2-nitrodiphenylamine (NDPA), dibutyl phthalate (DBP) and nitrotoluenes (DNT–TNT), which are present in small amounts in propellant I.

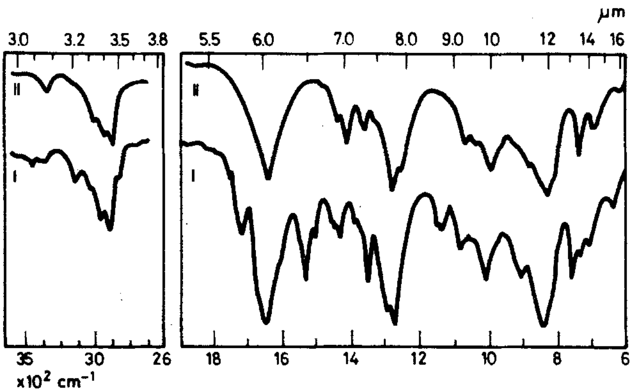

Fig. 2 IR spectra of the condensates obtained from propellant I and II at 130° recorded as smears between NaCl windows

The TG, DTG and DTA traces obtained on 5 mg samples at a heating rate of 10 deg min^{-1} are shown in Fig. 3. Discernible weight loss commences at around 110° for both propellants. The TG data on propellant I showed four distinct reaction regimes: a slow decomposition stage at 110–150°, followed by an accelerated decom-

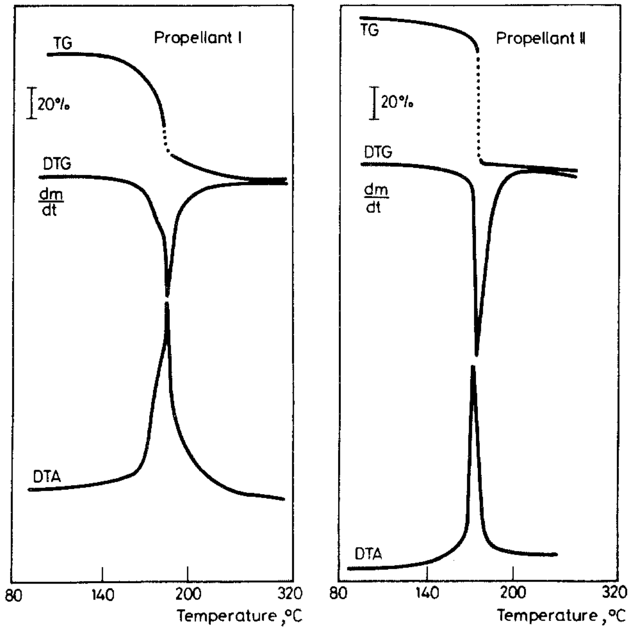

Fig. 3 TG, DTG and DTA traces in static air on 5 mg samples of propellants I and II at heating rate of 10 deg min^{-1}

position phase at 150–180°, culminating in an abrupt weight loss region due to ignition; this was then followed by a very slow decay period caused by oxidation of the carbonaceous residues. The total weight loss was 70% in air and 78% in N_2 atmosphere. Two exothermic peaks were observed in the DTA curve, the first broad one beginning at around 120°, with a maximum at 185°, and occurring as a broad shoulder on the second, sharp peak at 198°. DTG similarly showed two peaks in the corresponding regions, indicating a two-step weight loss process. For propellant II the weight loss commences at 110°, rapidly accelerates to 180°, and culminates in an abrupt weight loss due to ignition. The total weight loss was 85% in air and 90% in N_2 atmosphere. The single sharp exothermic peak in the DTA curve, at 110–220° with maximum at 180°, and the similar DTG curve in the same region, indicated a single-step decomposition process terminating in ignition. The weight losses were higher and the curves were sharper in N_2 atmosphere.

Ignition delay times (D_t) were measured in the temperature range 180–220° using 100 mg samples. The E values estimated from a plot of log D_t vs. reciprocal temperature using the equation [2, 3]

$$\log D_t = -\frac{E}{RT} + B,$$

were 80.6 kJ mol^{-1} and 93.7 kJ mol^{-1}, respectively, for propellants I and II. D_t and ignition temperature were found to depend on the sample mass. The results of D_t measurements on sample masses varying from 20 to 120 mg are shown in Table 4. The decrease in ignition temperature with increase in sample mass seems to indicate a self-heating effect. The increase in induction period (D_t) with increasing mass would imply that heat dissipation due to increased mass overrides the self-heating effect during the short interval in which ignition occurs.

Table 4 Ignition delay time (D_t) for 100 mg samples of propellants I and II at various temperatures, and dependence of D_t and ignition temperature (It) on mass of sample for propellant II

Temp., °C	Propellant I D_t, s	Propellant II D_t, s	Effect of mass of sample on D_t and It for propellant II Sample mass, mg	It, s	D_t at 190°, s
170	> 600	213	20	180	23
180	74	63	40	178	27
190	42	40	60	176	31
200	26	22	80	174	35
210	16	11	100	173	38
220	9	8	120	172	40
230	6	5			

Discussion

The E values obtained with the B & J and VST methods are tabulated in Table 5. For the B & J method the unimolecular rate law is closely applicable, whereas in the VST method this law is applicable only for the first phase of decomposition, ending with the acceleratory period. The E values obtained using the Jacobs–Kureishy [4] method, in which the E values calculated are independent of the kinetic equation, are also included in Table 5. The similarity in the E values obtained from the B & J and VST methods is understandable, since O–N bond breakage is the reaction expected in both methods during the acceleratory phase of decomposition. Thus, with the limitations of the E values and their dependence on such factors as experimental technique, method employed for evaluation, composition and nature of the sample, etc. are recognized, the values 134–139 kJ mol^{-1} for propellant I and 149.5–170.1 kJ mol^{-1} for propellant II are quite close to the thermochemical O–N bond energy of 152.9 kJ mol^{-1}. Hence, it appears that the initial step in the decomposition of DB propellants is the breaking of O–N bonds. In addition the fact that these E values are close to or within the range 35–46 kcal mol^{-1} (147–193.2 kJ mol^{-1}) reported by various authors [6–10] for the thermal decomposition of NC and NG would indicate that the mechanism of decomposition in these DB propellants is not significantly different from that of free NC and NG. The slightly lower E values obtained for propellant I, in spite of its low calorimetric value and lower N content of NC, may be attributed to the catalytic influence of inorganic additives present in the composition,

Table 5 Activation energy values for propellants I and II calculated using Arrhenius and Jacobs–Kureishy methods, kJ mol^{-1}

Decomposition technique	Temp. range °C	Propellant I		Propellant II	
		Arrhenius	Jacobs–Kureishy	Arrhenius	Jacobs–Kureishy
B & J	130–160	136.9	136.5	149.5	144.5
	100–120	–	–	311.4	–
VST	120–160	138.6	140.7	170.5	170.1
Ignition delay (D_t)	180–210		80.6		93.7

the role of which is to modify the ballistic characteristics of this low cal val propellant. The two-step decomposition process observed from the thermoanalytical curves for this propellant may also be due to the catalytic effect.

In the low-temperature range 100–130°, an E value of 311.4 kJ mol^{-1} was obtained for propellant II in the B & J method. The decomposition being very slow at low temperatures, the partial pressure of nitrogen oxides within the decomposition vessel will be too low to contribute to autocatalytic decomposition, whereas with the increased rate of decomposition at high temperatures, the autocatalytic effect will become significant. Autocatalytic decomposition in CHNO-type explosive is well recognized. This phenomenon would also explain the slightly higher E values obtained from VST studies, in which the pressure of the gaseous decomposition products are initially lower as compared to that in the B & J method. Further, the rate of decomposition in the VST method is monitored from the volume of total gaseous products, which at high temperatures would include oxidation products of the organic moities involving rupture of C–C and C–O bonds possessing higher bond energies. The rapid increase in the ratios of toal gas volume of NO with increase in temperature substantiates the above observation.

It is of interest to consider the E values of 58.8 kJ mol^{-1} and 378 kJ mol^{-1} for the temperature regions 90–170° and 170–205°, respectively, reported by Pai Verneker et al. [5] on the basis of TG data for a propellant of almost identical composition to I. They attributed the low E value (58.8 kJ mol^{-1}) to the diffusion of NG, and the species obtained by N–O dissociation, through the matrix. Although the diffusion process may be rate-controlling, particularly for samples of larger dimensions at lower temperatures, the observation in the present study that NG volatilization is significant during the initial stages of heating, and particularly in the lower-temperature region, tempts us to relate their low E value mainly to the vaporization of superficial NG and other volatile constitutents present in the propellant composition, the loss of which could be well accounted for in the TG data. The presence of NG as well as DNT–TNT, DBP 2–NDPA etc. in the condensate obtained from propellant I has been substantiated by IR data. A similar observation has also been reported recently by Pai Verneker et al. [11]. Further, it is worth-while comparing the E values of 80.6

to 93.7 kJ mol^{-1} obtained from ignition delay measurements in the temperature range 180–210° with the value of 90 kcal mol^{-1} (378 kJ mol^{-1}) reported by Pai Verneker et al. [5] from TG data for a similar temperature range. While the E value obtained from D_t measurements does have its limitations, such a large difference in the E values for the same temperature range seems surprising since the physico-chemical processes occurring during the two techniques are expected to be similar. Although we have no concrete explanation to offer for this discrepancy, it may be added that in this high-temperature region of 180–210° the decomposition reaction is very fast and ignition of the propellant occurs within seconds. Thus, while D_t measures the time to self-ignition of the product gases, the isothermal TG data also take into account the after-ignition weight losses associated with the oxidation reactions of the carbonaceous residues.

Conclusions

The physico-chemical processes occurring during thermal decomposition of DB propellants are influenced by factors such as the temperature range of decomposition, the chemical composition, the physical nature and the mass of the sample. Depending upon the experimental techniques employed, the reaction processes being followed vary. NG vaporization from the surface and slow uncatalyzed ON bond dissociation are the important reactions during the early period of heating in the low-temperature range 100–140°. As the temperature increases, autocatalytic accelerated decomposition becomes progressively predominant, resulting in fast reactions involving rupture of C–O and C–C bonds and ignition of the propellant at temperatures above 180°.

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Zusammenfassung — Untersuchungen der thermischen Reaktivität von zwei Treibstoffkompositionen, die sich in ihrer chemischen Zusammensetzung, in ihren kalorimetrischen Werten und in der ballistischen Charakteristik signifikant unterscheiden, wurden im Temperaturbereich von 100–160 °C ausgeführt. Der Zersetzungsverlauf wurde nach zwei Methoden verfolgt: (i) durch Bestimmung der Bildungsgeschwindigkeit von nach der Methode von Bergman und Junk in Freheit gesetztem NO; (ii) durch Bestimmung des entwickelten Gases nach der Vakuumstabilitätstestmethode. Die gemäß der Arrhenius-Gleichung und nach der Jacobs–Kureishy-Methode bestimmten Werte für die Aktivierungsenergie sind vergleichbar und liegen im Bereich von 134–170 kJ mol^{-1}. Im Temperaturbereich von 100–140 °C tritt während des frühen Stadiums der Erhitzung eine signifikante Verflüchtigung von Nitroglycerin ein. Oberhalb 180 °C verläuft die Zersetzung des Treibstoffs sehr schnell unter Verbrennung, woran sich eine langsame Oxydation des kohlenstoffreichen Rückstandes anschließt. Thermoanalytische Daten weisen darauf hin, daß der Treibstoff I in zwei Schritten, der Treibstoff II jedoch in nur einem Schritt zersetzt wird.

Резюме — В области температур 100–160° проведено исследование термической реакционной способности двух двухкомпонентных ракетных топлив, значительно отличающихся по химическому составу, калориметрическим показателям и баллистическим характеристикам. Процесс разложения был изучен двумя методами: а) определением скорости выделения NO по методу Бергмана и Джанка и б) определением объема выделяющихся газов методом испытания вакуумной устойчивости. Энергии активации, вычисленные на основе уравнения Аррениуса и по методу Джекобса–Карэйши, были аналогичны и находились в области значений 134–170 кдж • моль$^{-1}$. На ранних стадиях нагрева в области температур 100–140° происходило значительное выделение нитроглицерина. Выше 180° скорость разложения протекала очень быстро, что приводило к воспламенению ракетного топлива с последующим затем процессом медленного окисления обугленных остатков. Термоаналитические данные показали две стадии разложения для ракетного топлива I и одну стадию — для ракетного топлива II.