Thermal decomposition studies of catalysed double base propellants

HARIDWAR SINGH* and K R K RAO

Explosives Research and Development Laboratory, Pashan, Pune 411 021, India

Abstract. To understand the role of lead salts of organic acids in the combustion of double base rocket propellants, thermal decomposition behaviour of propellants was studied by DTA and TG methods. Catalysed propellants decomposed at lower temperatures than the control. Percent thermal decomposition of propellants containing lead salts was also higher. Rate constants were higher and energy of activation was lower for catalysed propellants. Results obtained suggest that condensed phase reactions may be the site for the action of lead salts in the combustion of double base propellants.

Keywords. Thermal decomposition; propellants; kinetic study.

1. Introduction

Lead salts of organic acids are reported to produce enhanced burning rates of double base propellants, followed by plateau burning in certain pressure region (Preckel 1961, 1962; Camp 1963; Henry *et al* 1966; Kubota *et al* 1973). Platonized propellants offer many advantages over conventional propellants and therefore, platonization and its mechanism are the subject matter of regular research (Camp *et al* 1954; Sinha and Patwardhan 1968; Kubota *et al* 1974; Lee *et al* 1978). Any catalyst or ballistic modifier to be effective should participate in, influence or modify the reactions taking place in various reaction zones. Many research workers hypothesised that surface and fizz zones are the likely site for the action of lead salts and reactions of luminous flame zone are less important. While studying the thermal decomposition products of organic lead and copper salts by mass spectrometer, Farber and Srivastava (1978) found that metallic salts of organic acids decompose to metallic elements, whereas organo-metallic compounds like tetraphenyl lead merely vapourise. They found that lead acetate, lead salicylate and lead-β-rescorcylate decompose to form H_2, H_2O, CO_2 and OH between 200–500°C. With lead acetate at 550°C, CO peak was more pronounced but was smaller than CO_2 intensity. At around 500–600°C, lead atoms were seen at fairly high intensity. The residue in the cell left after decomposition contained lead droplets and solid carbon. Eisenreich and Pfeil (1978) observed that propellants containing lead salts produce lower activation energy (E) and higher heats of reaction. Lead salts can influence the kinetics and/or energetics of the reactions of various zones. Hence, it appeared of interest to study the role of thermal decomposition of lead salts on the combustion of double base propellants.

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* To whom all correspondence should be addressed.

2. Experimental

Nitrocellulose (NC), nitroglycerine (NG), dinitrotoluene (DNT) and carbamite of required purity were obtained from Ordnance Factory. Lead salts of organic acids were prepared in the laboratory by precipitation method (Klare and Markley 1961). Propellant strands were prepared by solventless extrusion technique (Warren 1960).

Differential thermal analysis (DTA) of propellants and lead salts was carried out with an indigenously fabricated instrument having stanton Redcroft (UK) temperature programmer. Platinum/platinum-13 % rhodium thermocouples were used. Platinum crucibles were used as a container for samples. Alumina was used as a reference sample. Thermogravimetric analysis (TG) of propellants was carried out with the help of TG apparatus of Stanton Redcroft (UK) make. All experiments were carried out under atmospheric condition.

3. Results and discussions

During steady state burning of double base propellant, four distinct reaction zones, namely, foam, fizz, dark and luminous zones have been identified (Kubota *et al* 1974). Lead salts are expected to affect the reactions taking place in one or more of these zones. We have reported earlier that lead salts of aliphatic acids like lead acetate, lead palmitate, lead stearate, lead oxalate, lead succinate etc decompose in an exothermic mode in the temperature range 300–500°C (Singh *et al* 1982a). Lead sebacate decomposes between 204–500°C with peak temperature (Tm) at 483°C. Among lead salts of aromatic acids, lead salicylate decomposed between 344–462°C with peak temperature at 446°C, whereas lead phthalate decomposed between 353–563°C with peak temperature at 474°C. Lead methylene di-salicylate (LMDS) is reported to decompose between 230–325°C with peak temperature at 305°C (Singh *et al* 1982b). These results suggest that, in general, lead salts of organic acids decompose exothermally in the temperature range of 300–500°C, which is very close to the temperatures of surface and fizz zones. Hence, exothermic decomposition of lead salts is likely to affect the reactions of these zones.

The DTA results of propellants are presented in table 1. The control propellant decomposed between 150–179°C with Tm at 174°C, whereas propellants containing lead salts decomposed between 145–165°C, with peak temperatures varying between 155–158°C. We have reported earlier that propellants containing lead acetate, lead palmitate and lead oleate plus carbon black (0.5 part) decomposed exothermally in the temperature range 147–166°C (Singh *et al* 1982a). Thus, at very low rate of heating (3°C/min) propellants containing lead salts decomposed at lower temperatures than the control. In view of these observations, further experiments were carried out at higher rate of heating (5°C/min). Even at the heating rate of 5°C/min, catalysed propellants decomposed at lower temperatures than the control. When the experiments were carried out under nitrogen atmosphere (flow rate of 10 l/hr), the nature of thermogram was the same as under atmospheric condition. Thus, lower decomposition temperatures and higher heats of reaction of catalysed propellants (area under thermogram for catalysed propellant was higher than the control for the same weight of propellant) may be the probable reasons behind the catalytic effect produced by lead salts. Though these data were generated at lower temperatures and at lower heating rate than the

Table 1. Thermal decomposition temperatures of propellants.

Additives (2 parts per 100 parts)	Weight (mg)	Decomposition Temperature (°C)		
		Inception (T_i)	Final Temp. (T_f)	Peak Temp. (T_m)
(i) Heating rate − 3°C/min				
nil	17·6	150	179	174
Lead sebacate	18·3	145	162	157
Lead oleate	17·8	147	164	156
Lead-β-resorcylate	18·2	145	162	155
Lead phthalate	17·5	146	165	158
(ii) Heating rate − 5°C/min				
nil	16·0	157	181	180
Lead sebacate	15·6	153	168	166
Lead oleate	16·0	149	168	164
Lead-β-resorcylate	16·8	152	175	173
Lead phthalate	16·0	154	173	170

(Composition: NC-51·0, NG-37·0, Carbamite-3·0, DNT-3·5, DBP-5·5)
Maximum temperature − 500°C

Table 2. Percent thermal decomposition of propellants (TG).

Temperature (°C)	Control	Lead palmitate (2 parts)	Lead sebacate (2 parts)	Lead stearate (2 parts)	Lead oleate (2 parts)
Rate of Heating − 5°C/min					
110	5·0	4·5	4·5	4·5	4·5
120	8·5	8·0	8·0	10·5	10·5
130	15·0	14·0	11·0	22·5	16·8
140	22·5	22·0	13·5	37·5	41·0
150	30·0	30·0	16·0	47·0	48·0
160	33·5	36·0	18·5	54·0	60·0
170	36·5	40·5	22·5	69·0	70·0
180	40·0	43·0	27·5	—	—

(Composition: NC-51·0, NG-37·0, Carbamite − 3·0, DNT-3·5, DBP-5·5)

conditions of actual propellant combustion, still the results show the trend on the pattern of reactions occurring during combustion.

TG analysis of propellants containing a few selected lead salts was carried out to find out the effect of lead salts on the percent decomposition of propellants. The comparative results are given in table 2. It is seen that percent decomposition of propellants containing lead salts was higher, particularly in the temperature range of

140–170°C (near the ignition temperature of propellant) than the control. Lower percent decomposition in lead sebacate containing composition is an odd case and needs further investigation. This may be due to enhanced thermal stability of propellant, probably due to stabilization effect of lead sebacate on the propellant decomposition products.

From the results of weight loss of propellants at different temperatures for a fixed duration of 3 hr, two kinetic parameters namely, rate constants and energy of activation (using Arrhenius equation $E = 2{\cdot}3033\, RT_1 T_2 \log K_2/K_1 / (T_2 - T_1)$, where K_1 and K_2 are rate constants at temperatures T_1 and T_2, R is gas constant) for the thermal degradation of propellants were calculated for temperature ranges 130–150°C and 140–160°C. These two temperature ranges were chosen based on the consideration that double base propellants decompose/ignite between 140–160°C. Results are given in table 3. Rate constants were higher and energy of activation was lower for catalysed propellants than those for the control propellant.

Considering the results obtained from a semi-quantitative angle, the heat balance equation at the propellant surface can be given by (Rastogi *et al* 1977);

$$\dot{m} C_s (T_s - T_0) = \frac{\lambda_g (T_f - T_s)}{L} + \dot{m} Q_s \qquad (1)$$

Where, $\dot{m}$ = mass burning rate, C_s = specific heat of solid propellant, T_s = surface temperature, T_0 = ambient temperature, T_f = flame temperature, Q_s = net heat release for gasification of propellant, λ_g = average thermal conductivity of gas, L = thickness of the reaction zone.

Table 3. Kinetic parameters for the thermal degradation of propellants.

Additives	Temperature (°C)	Rate constant (K) (hr^{-1})	Energy of activation (E) (K. cal/mole)
Control	130	0·036	16·9
	150	0·097	
Lead stearate (2 parts)	130	0·049	14·6
	150	0·115	
Lead oleate (2 parts)	130	0·076	13·5
	150	0·171	
Lead sebacate (2 parts)	130	0·054	11·4
	150	0·107	
Control	140	0·063	53·5
	160	1·305	
Lead stearate (2 parts)	140	0·063	51·2
	160	1·146	
Lead sebacate (2 parts)	140	0·075	51·0
	160	1·328	
Lead oleate (2 parts)	140	0·065	51·7
	160	1·158	

(Composition: NC-51·0, NG-37·0, DNT-3·5, Carbamite-3·0, DBP-5·5)

To understand the role of the thickness of the reaction zone, the reaction zone may be considered as a continuous chemical reactor [volume $(V) = L \times$ area], where reactant gases are fed with certain velocity depending on the rate of thermal decomposition of propellant from the surface. The thickness of reaction zone represents the distance, which the reactants have to travel for the completion of gas phase reactions and hence smaller the reaction zone, faster will be the reaction. Therefore, if solid or gas phase reactions are catalysed, L would be smaller, implying increased burning rate. Higher rate constants and lower energy of activation for catalysed propellants (table 3) suggest that lead salts can reduce the thickness of reaction zone considerably, accounting for higher burning rates.

4. Conclusion

Lead salts of organic acids decompose exothermally in the temperature range 300–500°C, which is very close to surface temperature of double base propellants. Propellants containing lead salts decompose at lower temperatures than the control. The per cent thermal decomposition and rate constants were higher for modified propellants. Energy of activation (E) was lower for catalysed propellants.

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