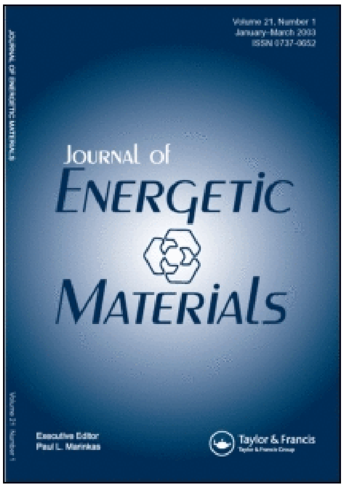

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Thermolysis of AP-additive mixtures, III[1]

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Thermolysis of ammonium perchlorate (AP) in presence of additives such as $CaCO_3$ and CaO has been investigated by ignition delay, DTA, and photomicrography techniques. The ignition delay, ignition temperature, and decomposition temperature and activation energy are found to decrease when CaO was incorporated in AP. However, $CaCO_3$ affected the ignition of AP at higher temperatures (621-770°K) but very little effect was observed at lower temperatures ($<$ 623°K). Thermolysis of AP seems to proceed through condensed phase reactions in presence of CaO and $CaCO_3$ and role of these additives in the deflagration and decomposition of AP has also been discussed.

The role of metal oxide additives (catalysts) in the deflagration and decomposition of AP has been described by many workers (1-7) but not much work seems to be reported on the effect of inhibitors (additives) (refs. 3,8-12). Various salts of ammonia, halogenides of lead and cadmium; mixture of ammonium salts and halogenides have been found to inhibit the deflagration rate (3,11,12) of AP. Glaskova has suggested following three steps for the inhibitory action of additives in the deflagration of AP :

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(i) Since ammonium salts liberate ammonia on decomposition which shift the AP decomposition equilibrium to the left.

(ii) Some additives bind $HClO_4$ and/or AP to less reactive compounds and,

(iii) $HClO_4$ decomposition is inhibited.

However, it should be noted that inhibitory action was even observed with very small concentration of additives (1%) and hence shifting of equilibrium would be very marginal and explanations (ii) & (iii) seem quite plausible.

Understanding of basic thermal initiation mechanisms is necessary to fully account for the combustion/explosion behaviour of propellants/explosives (13-18). If the heat produced by the decomposition of an energetic material cannot be dissipated as rapidly as it is liberated, the charge will self heat to ignition or explosion. If activities of the reactants do not change significantly during pre-ignition reactions, the logarithm of the time of ignition (t_{id}) should be a linear function of the reciprocal of the absolute temperature. Some workers (19-21) have proposed the following relation (Eq.1) which has been found to be obeyed by a large number of propagatively reacting systems such as explosives (22-25) and propellants (1-3).

$$t_{id} = A\, e^{Ei/RT} \qquad - \qquad (i)$$

Where A is a function of the activity of reactants, T is the absolute temperature, and E_i is the energy of activation (ignition).

The complexity and transient nature of the surface reaction zone makes experimental measurement nearly impossible to conduct under combustion condition. Therefore, it has been helpful to gain insight in the deflagration mechanism by using techniques that attempt to simulate some of the conditions (26). The objective of the present investigation was to examine the role of inhibitors (additives) such as $CaCO_3$ and CaO in the thermolysis of AP (studies on catalysts are published in refs. 1 & 2). Therefore, DTA, ignition delay (under rapid heating condition) and photomicrography studies in the presence and absence of inhibitors, were undertaken. The results suggest that condensed phase reactions are predominantly responsible for the thermolysis of AP in presence of $CaCO_3$ and CaO.

Experimental

Materials

AP (Central Electrochemical Research Institute, Karaikudi, Tamil Nadu) 100-200 mesh; $CaCO_3$ and CaO (Merck) (200-400 mesh) were used as received.

DTA studies on AP and AP + additives

DTA studies were carried out in static air at ERDL, Pune, using 10 mg (100-200 mesh) of each sample at a heating rate of

10°C/min. The differential thermograms were recorded using a two pen strip chart recorder. Sample were placed in a thermocup (Pt) and Al_2O_3 was taken as reference material. Pt-Pt (Rh 13%) thermocouple was used for recording the ΔT. The DTA thermograms for AP+ additives are presented in Figure 1.

Ignition delay measurement on AP with and without additives by hot plate (HP) technique

100 mg of the sample (additive concentration = 4% by wt.) in the powder form was taken in a corning glass cup (dia=2 cm and height=4 cm) and ignition delay was measured by the usual method as described earlier (1,2). The mean of the four runs was taken to be t_{id} showing less than ±5% variation at each temperature and the data are reported in Table 1.

Ignition delay measurement on AP with and without additives by tube furnace technique

50 mg of the sample (additive concentration = 0.5% by wt.) in the powder form was taken in a ignition tube (height = 5 cm and dia=0.4 cm) and ignition delay was measured by the same procedure as reported earlier (1,2). The variation in t_{id} values (four runs) was less than ±5% and ignition delay data are reported in Table 1.

Results and discussion

The decomposition temperatures (T_d) were found to be lowered as compared to pure AP when CaO and $CaCO_3$ were incorporated in

AP (Table 2). Very sharp peaks (exotherm) are observed for the laters (Figure 1). These additives have also been found to lower the ignition delay (t_{id}) of AP in HP technique upto 770°K and above this temperature, t_{id} is ennanced slightly (Table 1).

While taking ignition delay data, AP gave melt (visible to naked eye) in presence of these inhibitors ($CaCO_3$ & CaO). Flickering flame was also observed in this temperature range with higher percentage of inhibitors. The amount of melt formed was found to increase with the increase in percentage of additives (10, 20 & 30%). In order to supplement the formation of melt, the samples of AP, AP + $CaCO_3$ (4%) and AP + CaO (4%) were photomicrographed after heating these samples (10 mg each) on slides, at 573°K for half an hour (Figure 2). On careful examination of the photomicrographs it seems that AP + additive samples have melted whereas clear particles are visible in case of pure AP which is reported to decompose without melting (27).

The formation of melt seems plausible on account of the formation of an eutectic mixtures of AP with $Ca(ClO_4)_2$ which might have been produced as follows :

$$2NH_4ClO_4 + CaCO_3 \longrightarrow Ca(ClO_4)_2 + CO_2 + H_2O + 2NH_3$$

$$2NH_4\ ClO_4 + CaO \longrightarrow Ca(ClO_4)_2 + 2NH_3 + H_2O$$

Schumacher (28) has also reported the formation of $Ca(ClO_4)_2$ as given above. AP decomposition seems to proceed at a much faster rate due to condensed phase reactions which will facilitate the release of NH_3 and $HClO_4$ (decomposition products of AP). This process continues upto 770°K and ignition delay was increased at higher temperatures (>770°K). It seems that liquid melt is finished at higher temperatures and t_{id} start increasing on account of the presence of thermally stable species such as $CaCl_2$ which might have been formed as decomposition product of $Ca(ClO_4)_2$ (d.543°K, ref. 28). The thermally stable species ($CaCl_2$) might reduce the heat and mass transfer at the thermolysing surface of AP and consequently ignition delay is enhanced. It is also interesting to note that both these additives form a measurable amount of thermally stable $CaCl_2$ (m.1055°K).

While taking ignition delay data with TP technique, it was found that t_{id} is slightly lowered in case of AP+CaO whereas it is slightly enhanced for AP+$CaCO_3$ in the temperature range 573-623°K (Table 1). It seems that CaO is better additives for condensed phase reactions. Moreover, $CaCO_3$ is acidic and CaO is highly basic in nature and possibility of formation of $Ca(ClO_4)_2$ would be much higher with the later than the former at lower temperatures. Smell of ammonia was observed when AP was mixed with CaO even at room temperature. Thus, $Ca(ClO_4)_2$ formation in case of CaO would lower the ignition delay at lower temperature as compared to $CaCO_3$.

In order to investigate the effect of additives on activation energy or ignition energy (E_i) for the deflagration of AP, ignition delay data were fitted in equation (1) and linear plots are obtained (Figures 3 & 4). E_i values (Table 2) are found to be lowered for AP+CaO (HP technique). However, not much variation was observed for AP+$CaCO_3$ (TF technique).

The trend in lowering of E_i is the same whether the data were taken with HP or TF techniques. Data obtained by HP and TF techniques cannot be compared because of the altogether different geometrical shapes and heating conditions. In the HP technique the sample is being heated up from the bottom side only, whereas in the TF technique the sample gets heated from all sides and ignition temperatures are lowered. (HP temp. range was 622-871K and TF temp. range was 573-623K). Further, it is well known fact that kinetic parameters vary with experimental conditions, even if the decomposition mechanism do not change, and it is described as kinetic compensation effect (29).

Conclusions

$CaCO_3$ and CaO have been found to lower the ignition delay, ignition temperature and energy of activation of AP at higher temperatures. Thermolysis of AP seems to proceed through condensed phase reactions in presence of CaO and $CaCO_3$, CaO is better deflagrating additive for AP as compared to $CaCO_3$.

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TABLE 1. Variation of ignition delay (t_{id}) with temperature for AP with and without additives.

Technique	Temp. (°K)	Ignition delay (sec.)		
		AP	AP+CaO	AP+$CaCO_3$
Hot Plate	622	DNI	70	88
	651	DNI	35	56
	682	DNI	30	50
	723	76	23	37
	747	58	21	35
	770	41	20	30
	793	21	19	28
	815	17	18	26
	838	16	18	24
	871	13	18	19
Tube Furnace	573	122	106	171
	583	106	94	132
	598	78	68	82
	613	66	57	78
	623	58	46	59

DNI - Did not ignite.

TABLE 2. Kinetic, and DTA, parameters for AP with and without additives

Sample	Activation energy (E_i) kcal mol^{-1}		DTA Peak definition temperatures, °C		
			T_i(on set)	T_d(peak)	T_e(offset)
	Hot plate technique	Tube furnace technique			
AP	19.2	14.1[a]	337	373	400
AP+CaCO$_3$	5.8	13.3	310	343	380
AP+CaO	3.0	12.3	305	340	370

[a] Data taken from reference 1.

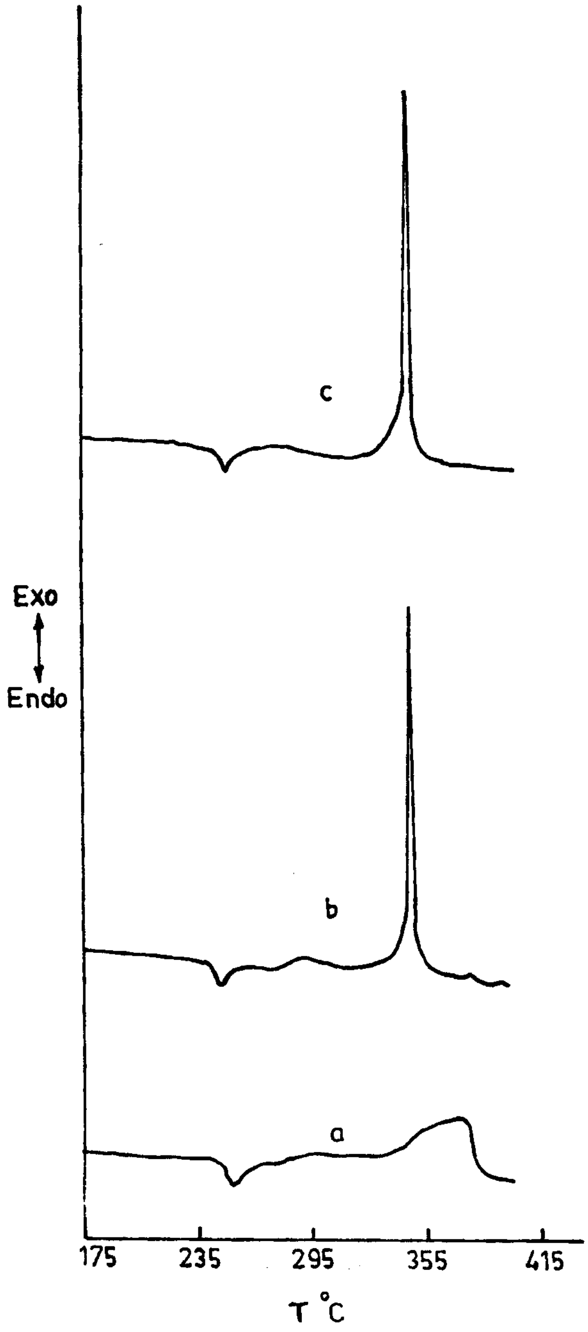

Fig. 1. Derivatogram for AP and AP + additives. (a) AP (b) AP + $CaCO_3$ (c) AP + CaO.

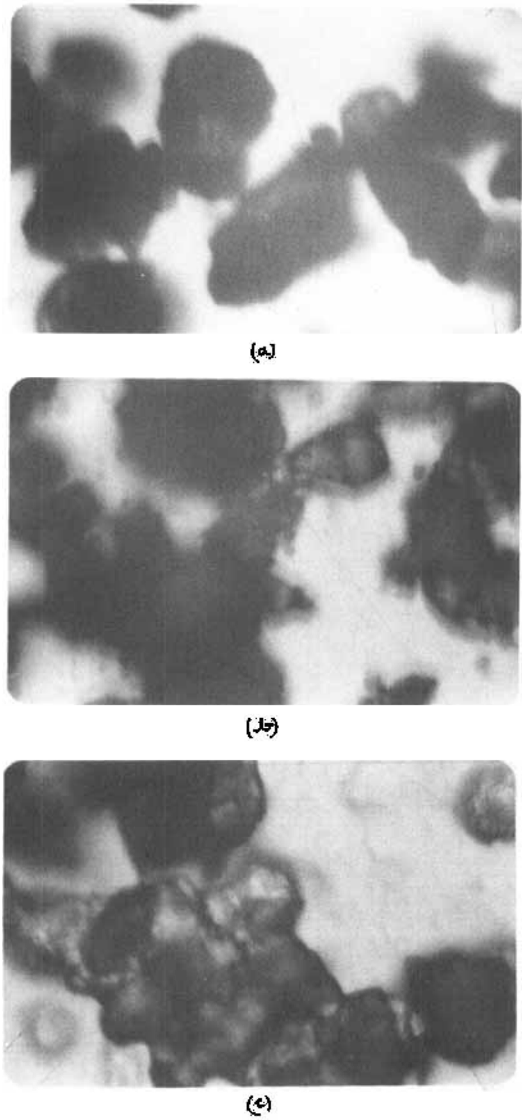

Fig.2. Photomicrograph, made with Research Microscope (NIKKEN TOKYO, Model No. TRM-3 (10x15)), for samples heated at 573K for 30 minutes (a) AP (b) AP + $CaCO_3$ (4%) and (c) AP + CaO (4%).

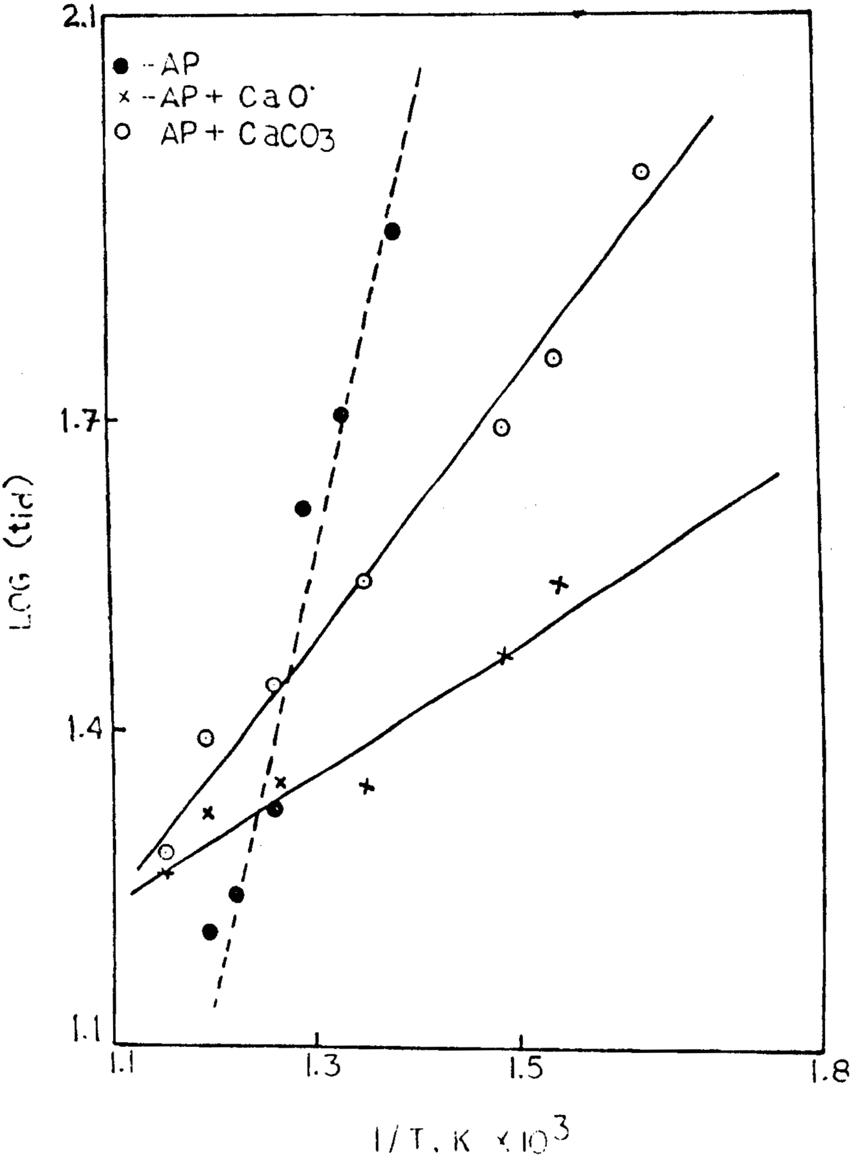

Fig.3. Plots of log(t_{id}) vs 1/T for AP + additives(hot plate technique).

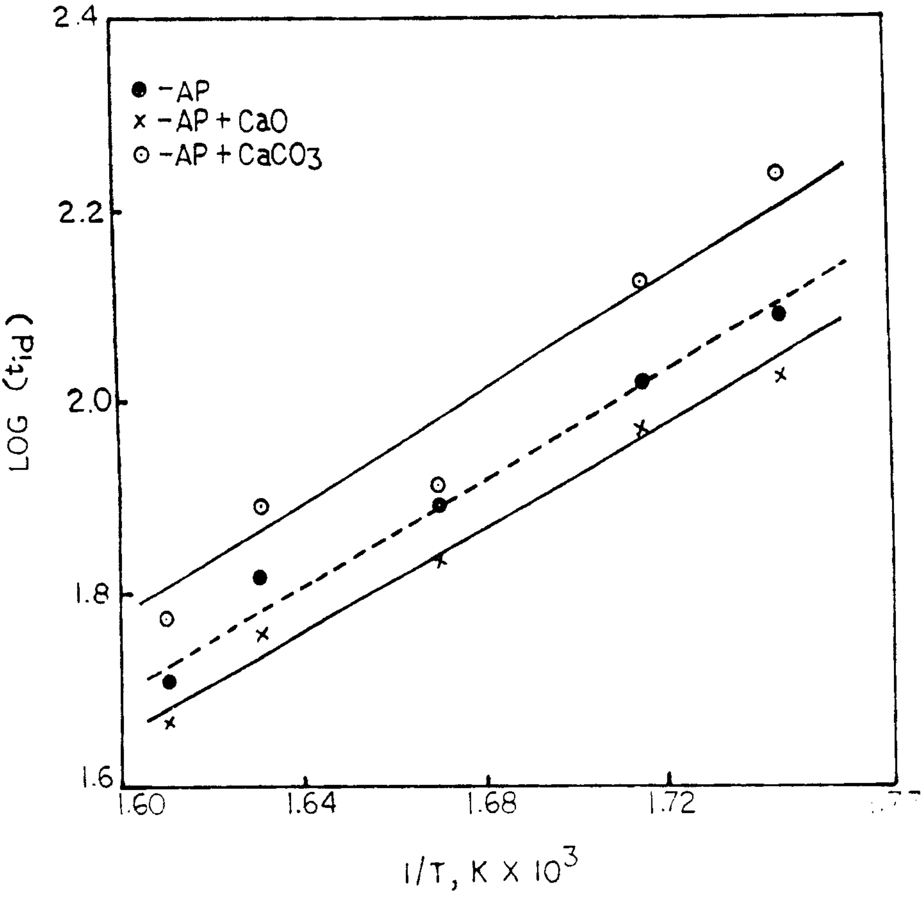

Fig.4. Plots of log (t_{id}) vs 1/T for AP + additives (tube furnace technique).