A REVIEW ON DECOMPOSITION/DEFLAGRATION OF OXIDIZER AND BINDERS IN COMPOSITE SOLID-PROPELLANTS

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Binder and oxidizer decomposition play very significant role during the combustion of composite solid propellants. Ammonium Perchlorate (AP) is the practical oxidizer in composite propellant formulations. Available information on binder decomposition in general and AP decomposition in particular have been collected and reviewed from the viewpoint of their application in propellants. This review may be useful in understanding the mechanism of propellant combustion.

Inorganic Oxidant[1,2] and polymeric binder[3] are the major components of the composite solid propellant formulations. By changing the chemical nature of either of them, the propellant properties are drastically altered. It has been shown earlier[3] that the binder decomposition temperature is related to the propellant burning rate. Similarly, it has been shown that AP deflagration[4] and decomposition[5–8] play significant role during the combustion of propellant. Glaskova[9-10] has shown that those salts which desensitize the decomposition of the AP also desensitire the deflagration of the AP. Recent work[11] in our laboratory on the similar salts have shown that they decrease the decomposition and burning rate of the propellant and also improve the ageing characteristics. Above examples very clearly exhibit the importance of binder and oxidizer decomposition and deflagration. It is, therefore, necessary to understand the decomposition and deflagration of the binder and oxidizer in depth separately. To bring the matter together and to evaluate the data on the above aspects forms the objective of the present review. It must be mentioned here that such an attempt has not been made so far in the past.

COMBUSTION AND DECOMPOSITION OF BINDERS*

Binder Combustion

In a polymer combustion[12] the material is initially heated in oxidising atmosphere with the help of some external source which degrades to give volatile products. Depending upon the combustibility of volatiles and the rate of their formation the material gets ignited with the help of an external heat source and then burns at a given rate. If the heat feed back from the flame to burning surface is sufficient the combustion becomes self-sustained. The steady state combustion of a polymer is a very complex process which includes the rate of evolution of pyrolytic gases, the rate of mixing with O_2 the rate of reaction with O_2 the finally the heat feed back to the polymer.

The processes of reaction in polymer combustion can be classified into (*i*) Gas-phase (*ii*) Surface and (*iii*) Sub-surface condensed phase. Basic knowledge about the combustion of polymers has been summarised by Fristrom[13] in his recent publication. The chemistry of gas-phase reaction is considered similar to the diffusion flames of hydrocarbons and substituted hydrocarbon mixtures. The least understood are the reactions occuring at the surface which may be liquid or solid char. The chemistry of such interfacial region differ considerably from that of thermal induced pyrolysis in the bulk of the polymers. Solid phase or condensed-phase reactions are those which occur on account of degradation. No mathematical model or comprehensive theory is available which describes the linear regression of polymer strand in an oxidizing atmosphere.

Condensed-phase Reactions If : the polymers contain no dissolved free radicals or oxidizing species pure thermal initiation requires the rupture of $C—C$ or $C—Z$ bonds with a high E ($\sim$50—100 Kcal mole^{-1}). The subsequent depropagation results in either gaseous products or cross-linking with char formation. The mechanism of char formations involves cross-linking and also the formation of conjugate double bonds followed by cyclisation and then dehydrogenation. UV sources can also initiate chain breaking and radical production of polymers.

The contribution of the condensed-phase reactions in the polymer combustion is precisely not known. However, following specific examples clearly demonstrate the importance of condensed-phase reactions.

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* for notations please see page 5.

Fennimore and Martin[14,15] studied the effect of Cl_2 and HCl on combustion of polyethylene and other plastics. They inferred, on the basis of oxygen-index measurements, that Cl_2 when chemically bound to the polymer retarded the combustion much more effectively compared to when Cl_2 is added to atmosphere around the burning polymer. Fennimore and Jones[16] studied the polymer flammability in two different oxidising atmospheres ($N\ O+N_2$) and (O_2+N_2) and found that the nature of the combustion behaviour of the polymer containing $Al\ O_3.\ 3H\ O$ filler was same in both the cases. Fennimore and Jones[16] also studied the combustion of the two polymers having similar Cl_2 contents [PVC and Poly 3, 3' bis (chloromethyl) Oxetane] and found that the oxygen-index of the two was vastely different showing that polymer combustion strongly depends upon polymer structure.

Martin and Rice[17] studied the effect of $Al_2O_3.\ 3H_2O$ and Al_2O_3 on the combustion of epoxy resins. $Al_2O_3.\ 3H_2O$ was found to increase oxygen-index tremendously after 40% loading. Anhydrous Al_2O_3 acted only as an inert filler. These results supported the occurence of condensed-phase reaction in polymer combustion. The authors also have shown that various phosphorous additives in epoxy resins retard the flame in condensed-phase. It is also well known that various phosphorous and boron compounds significantly increase the char formation in the condensed-phase. According to Boilat *et. al.*[18] the combustion of PU foam is controlled by a combination of vapour and solid-phase mechanisms. Phosphates modify the solid-phase mechanism while non reactive PO_4 and Phosphine oxides are active in the vapour-phase. According to Yoshinage *et. al.*[19] inorganic additives in PVC increase its ignition temperature by either an inhibiting effect in the vapour phase by thermal decomposition or in the solid-phase by a shielding effect. H_3PO_4 which is converted into $(H_3PO_4)_n$ showed a large solid-phase effect on flammability.

Kwan-Nan Yeh et. al.[20] determined the effectiveness of H_3PO_4, $(NH_4)_2HPO_4$, and tetrakis-(hydroxymethyl) phosphenium hydroxide as fire retardant on cotton from rate of heat release data. These retardants acted in the solid-phase by reducing the amount of fuel evolution into the gaseous-phase.

Binder Decomposition

Uncatalysed Decomposition of Binders.—Compared to the considerable effort that has been devoted to understand the AP decomposition, binder decomposition has received very little attention[21]. This may be due to the fact that the oxidizer, which is present in large quantity in propellant, may perhaps control the combustion characteristics. However, with the advancement of the combustion modelling and tailoring the need of binder decomposition during the combustion has been recognized.

According to Adams and Co-workers[22] the burning rate of AP based composite propellants is usually independent of the chemical characteristics of the binder in the low pressure region (below 100 psi), the binder characteristics have marked impact upon propellant burning rate and pressure exponent. Although lot of studies are available on the kinetics and mechanisms of the thermal degradation of the variety of polymers, almost negligible effort has been made to understand the binder degradation relevant to the propellant combustion. Thermo-oxidative decomposition has been studied by Beachell and Nemphos, Grassie and Weir, Notely, Parker, Ryan and Hawkins for a variety of polymer systems[26,32]. The principal results of these studies are :

1. Significant surface regression of polymers appears to start around 300°C.

2. Endothermic pyrolysis reactions may occur below 300°C which do not result in significant weight loss of polymers.

3. Exothermic oxygen-polymer reactions apparantly occur before ignition.

4. Ignition in oxygen appears to start when regression of polymer begins.

5. Results of the fast pyrolysis reactions appear to be reasonable extrapolations of the results from conventional tests.

Howard[23] measured relative rates of gasification of propellant fuel binders at temperatures near to that encountered at the gas-solid interface of a burning propellant. The rates of gasification of the polymer were studied at 350°C to 475°C in glass vacuum line. He found that the rate of pyrolysis of the fuel-binders follow the following order: Polyester-PU rubber, poly isobutene, polyether-PU rubber. He also suggested to seek a correlation between fuel pyrolysis characteristics to the burning rate of the propellants based on those fuels, Arendale[24] suggested that, since the polymeric materials act as a fuel in addition to their function as a binder the combustion enthalpy or fuel value of polymer is an important factor in obtaining a propellant formulations of maximum energy per unit weight.

Cohen and Co-workers[25] determined the heat of decomposition by using the method given by Shannon[23]. This method uses the energy balance principle where a plot is made between specific weight loss versus specific total energy delivered. The slope of the plot is inversely related to the effective heat of decomposition. The effective heat of decomposition, in turn, is equal to the sum of the energy required to achieve the surface temperature and the heat of decomposition. Heat capacity of the material and surface temperatures are known from separate measurements. Table 1 summarizes the heat of decomposition data and E values for different currently used polymers as binder in propellants. PU has the lowest heat of decomposition while flurocarbon has the highest.

Using DSC technique Varney and Strahle[27] determined the heat of decomposition for several polymeric binders. The values are given in Table 1. They also determined the binder degradation kinetics by using the same technique and found that the binders follow a first order rate law. The E values are given in Table 1. A discrepancy in the heat of decomposition values obtained by Cohen et.al.[25] and Varney et.al.[27] is evident. It is difficult to find the exact cause for this divergence. Cohen and Co-workers[25] have said that the difference in heat of polymer decomposition will have small effect on the binder surface temperatures for given propellant $\dot{r}$.

Bouck et al[28] studied the mechanism of pyrolysis and oxidation of nine ploymeric fuel binders (typical of those used in composite propellants) at high heating rates by using DSC. They found that the mechanism at high heating rates was different from that predicted by low heating rates and in either case energy effects were small compared to oxidation effects. They also found that the oxidation by gaseous oxygen or by the decomposition of admixed AP indicated an exothermic reaction below the sample ignition temperature.

TABLE 1

DECOMPOSITION ENERGETICS

Binder	Heat of Decomposition[25] (cal/g)	Heat of Decomposition[27] (cal/g)	E (Kcal/mole)
CTPB	381	1,910	28
HTPB	433	..	..
PBAA	..	1,950	34
PBAN	564	..	..
PU	260	77	61
Flurocarbon	1,004	..	..
Polysulfide	530	66	78
Talagen-S	760	..	..

Varney and Strahle[27] used heat of decomposition for calculating the binder surface temperatures during deflagration. Their results were in good agreement with experimentally observed surface temperatures. These results strongly suggest that the binder plays a significant role during the combustion of the propellants.

Rabinovitch[29] described a method for calculating the $\dot{r}$ of simple polymeric fuels (PS, PMMA, and PE) in hybrid operation by thermal degradation data. The agreement between calculated and experimentally observed $\dot{r}$ was very good. He also extended his calculations to derive theoretical $\dot{r}$ for composite propellants containing these binders and oxidizer AP or $KClO_4$. The results were not in agreement with the experimental values. He attributed this discrepancy due to the lack of the appropriate data on the oxidative degradation of polymers in the presence of O_2 and other oxidizing species like Cl_2, NO_2, NO etc., which are formed due to the oxidizer decomposition.

Kishore et al[30] have studied the thermal degradation of PS. They have obtained a value of 300 Kcal/mole for the activation energy which was independent of the technique employed. Their data on the kinetics support a chain end initiation and unzipping process. Kishore and Pai Verneker[31] have shown a correlation between the heats of depolymerization and activation energies in the degradation of polymers. It was found that the heats of depolymerization of the polymers were of almost same as the activation energies for their degradation suggesting thereby that degradation takes place in the following way.

$$\text{Polymer (solid)} \xrightarrow[\text{E}]{\text{primary reaction}} \text{Monomer (gas)} \xrightarrow[\text{Reactions}]{\text{Secondary}} \text{other products}$$

Unfortunately, the majority of the polymer investigations[32] cited have been performed under the classic conditions of slow heating rates or isothermal conditions in vacuum environments. However, the residence time of a polymer element at the solid surface during the normal ignition and combustion of a solid propellant is usually of the order of milli-seconds. Thus, a major portion of the heating and reaction sequence will involve transient processes. Furthermore, the pressure level is normally several hundred pounds per square inch in most actual combustion environments. Direct application of the low-pressure iso-thermal decomposition data to the propellant combustion is questionable. In addition, it is likely that the rate of the surface degradation produced by intense surface heating is quite different from heat controlling bulk degradation. The need for additional studies of polymer decomposition at rapid heating rates, high pressure and transient conditions is desirable.

Catalysed decomposition of binders: It is well-known that metal salts can act as accelerators for hydrocarbon exidation[33] and can lower the activation energy for hydroperoxide decomposition. Some metallic salts, e.g. Cupric stearate, are capable of lowering an apparent E of the auto-oxidation from 30 Kcal. mole^{-1} for the neat polymer to about 24 Kcal. mole^{-1} for the metal containing polypropylene. The order of decreasing catalytic effect of the fatty acid metallic salts is as follows, based upon oxygen absorption curves and activation energy:

$$Co > Mn > Cu > Fe > V > Ni > Ti > Al > Mg > Ba$$

Metal catalyst activity during polyolefin auto-oxidation has been correlated with the redox potential of the various metals studies. Thus the following reaction have been postulated[33].

$$RO_2H + M^{n+} \longrightarrow R\dot{O} + H\dot{O} + M^{(n+1)+}$$

$$ROOH + M^{(n+1)+} \longrightarrow R\dot{O}_2 + H^+ + M^{n+}$$

From the above equations it can be seen that the ability of metals to decompose hydroperoxides may depend upon their redox potential. Osawa and Co-workers[34] found that metal catalyst activity can be correlated well with redox potential. Stivala and Co-workers[35] found a correlation when log (Pm-Po) versus redox potential is plotted for various metal salts e.g. Cobaltic, Manganic, Ferric and Cupric, during the auto-oxidation of films of APP at 100°C and 100% oxygen, where Pm and Po denote maximum rate of carbonyl formation in presence and absence of catalyst respectively. The order of catalytic effect was similar to that observed by Osawa and Co-workers[34]. However, contrary to the results obtained in solid state auto-oxidation of APP, Chaudhary[36] found that the cobalt salt was the best effective, followed by *Ni*, *Fe*, *Mn* and *Cu* (the activity increasing in this order). This reversal of catalyst activity was attributed to the medium.

DEFLAGRATION AND DECOMPOSITION OF AMMONIUM PERCHLORATE (AP)

Deflagration of AP: The self-deflagration rate of AP at typical pressures is of the same order as the $\dot{r}$ of many AP-based propellants. Thus, the AP deflagration may well be a controlling factor for propellant $\dot{r}$. The deflagration of pure AP has been investigated intensively in an effort to gain a basic understanding of this process and hence of the combustion of rocket propellants that contain AP as the oxidizer. These studies have proceeded along two directions: (*i*) investigation of the effects of pressure, additives and added radiant energy on the $\dot{r}$ (*ii*) study of the chemistry of the deflagration process.

Deflagration pressure limits: AP undergoes self sustained combustion only in certain pressure ranges, giving rise to pressure limits. The existence of non-deflagration pressure ranges where steady deflagration does not occur, is one of the most interesting aspects of AP deflagration which has so far managed to clude explanation. Generally, such a range is found to be below a certain pressure level known as the low-pressure deflagration limit (LPL) and above a certain pressure level known as upper pressure deflagration limit (UPL). Of these two limits, the LPL has greater practical importance and has been the subject of many theoretical and experimental studies and no satisfactory model, which can explain and predict the LPL, is available. By contrast, the UPL has not been systematically studied.

Friedman et al, Hightower and Price, Horton and Price, Levy and Friedman, Watt and Peterson from their data[1,2] have decided the average value of LPL 20 atm and $\dot{r}$ under their conditions is around 0·2—0·3 cm/sec for single crystal or high density pellets. Johnson and Nachbar[37] found that (*i*) LPL is insentive to sample size and inert atmosphere (He, N_2), (*ii*) LPL increases as the particle size is decreased, (*iii*) LPL is lowered as pre-heating and (*iv*) LPL rises on pre-cooling. Cohen Nir[38] also found that LPL increases as the particle size is decreased. He also observed that LPL decreased with increasing pellet density, burning surface area and sample initial temperature.

Details of microstructure : Hightower and Co-workers[1,2,39] discovered the presence of molten surface which was later confirmed by scanning electron microscopic studies. They found the (*i*) Surface temperature was 550°C — 600°C and (*ii*) even after quenching the gas bubbles came out showing that gasification occurs below the melt, however, the major decomposition occurs in melt. They concluded that the melt plays a significant role in AP deflagration as it provides a large area for heat transfer and gives opportunity for both gas-phase and heterogeneous reaction. Boggs and Kraeutle[40-41] and Cohen Nir[42] confirmed the presence of liquid melt. Boggs and Kraeutle[40–41] found that the thickness of melt layer decreases by increasing the pressure. Below 900 psi the whole surface was covered with liquid and gasification was occuring below the surface. Boggs[43] experimentally measured the melt layer thickness and found it to be 2-5 microns depending upon pressure. He observed that between 20-50 atm. the gases remain entrapped in the melt and between 50-100 atm. surface was covered by a pattern of ridges and valleys with sites of increased activity at the bottom of valleys. However, Guitao and Williams[44] believe that thickness of liquid layer decreases by increasing the pressure.

Mechanism of pressure limits : Among the few attempts to explain the self quenching phenomena at low pressures most often cited is the mathematical analysis of Johnson and Nachbar[37]. In their analysis which alone could not predict LPL, they added an arbitrary heat loss term from the solid phase. When this term was given a very large value, which is impossible from the known physical grounds, self quenching could be predicted. They also concluded that the radiant-heat losses from the gas-phase as calculated by Olfe and Penner[45] and from the burning surface, were too small to account for the observed LPL. Maksimove et al[46] Hightower and Price[2] all believe that liquid melts act as a heat sink and when its thickness becomes too large self quenching takes place. This gets credence from the fact that melt layer thickness increases by decreasing the pressure. Guirao and Williams[44] said that self-quenching occurs when liquid layer disappears (according to them liquid layer does not exist at low pressure below LPL) as a result the surface temperature falls below the melting point of AP. Sohn[47] theoretically predicted that self-quenching occurs on account of 2 or 3 dimensional heat losses. The exact quantitative explanation for observed LPL still remains to be explained even today.

Effect of additives on pressure limits and regression rate : LPL has been found to be very sensitive to catalysts. Friedman et al[48] found that 3 wt% of CuO. Cr_2O_3,Fe_2O_3,MnO_2 increase LPL while copper chromite when present in large quantity decreases the LPL while small quantity increases. Shamgin and Shidlovskii[49], found that 3 wt% MnO_2, 5 wt % $KMnO_4$, 2 wt % $CuCl_2 . 3H_2O$, lowers the LPL. According to Friedman et. al[48] there are two process which occur in presence of catalysts (*i*) increase in the radiative feed back to the surface (*ii*) increase in the radiative heat loss from the surface. Coupling the two shows that at low concentration of the catalyst heat loss is dominant and heat feed back is less. At high concentrations catalysts catalyse the exothermic reactions and hence heat feed back outweighs the heat loss effects. He supported his arguments from the fact that the LPL decreases when radiative energy from and external source is allowed to fall on the burning surface. Sohn[50] said that catalysts change LPL probably by influencing the surface microstructure. Cohen Nir[42] found that Cu_2O sensitizes the deflagration of AP because it gives rise to exothermic reactions with the products of AP decomposition. Some of the important observations on the deflagration of AP are as follows :

1. The LPL decreases with increasing the strand density, the burning surface area and the sample intial temperature.

2. The internal structure of an AP pellet compressed during several hours is different from that of a pellet compressed briefly. In the first case the structure is more uniform and homogeneous, the volume of the voids is probably reduced. Heat losses due to voids are then less important and AP deflagration can be maintained down to nearly 20 atm.
3. LPL decreases as the particle size of AP increases.
4. Lower concentrations of the catalyst increase the LPL while higher concentration decrease it.

Glaskova[51] has investigated the effect of catalytic additives on the combustion of AP and its mixtures with cake. Catalysts employed were $K_2Cr_2O_7$, Cr_2O_3, and Fe. The greatest catalytic effect on both AP and its mixture was with $K_2Cr_2O_7$.

Shadman-Yezdi and Peterson[52] have investigated the effects of $KMnO_4$, Fe_2O_3, CuO and Copper Chromite on the pressure limits of combustion of AP. The LPL in all the cases increased with small additives of each catalyst and then decreased at higher concentrations of the catalyst. They showed that the catalysts become more effective when its particle size decreases. According to them catalysts effect both condensed-phase and gas-phase reactions. Shadman-Yazdi[53] developed a theoretical model to explain the existance of pressure limits in the deflagration of AP. The effect of catalysts can be explained qualitatively by this model.

Shadman-Yazdi[54] has studied the ignition of pellets of AP containing different concentration of catalysts ($KMnO_4$, Fe_2O_3, CuO and Copper chromite) under nitrogen pressure. From the results a 2 step series reaction model has been developed assuming that the first step to be an endothermic reaction producing intermediate products and that the second step to be an exothermic reaction leading to final products. At low catalyst concentrations the rate of the endothermic step is predominant, at high catalyst concentration the rate of the exothermic step becomes predominant and the LPL decreases.

Recently Boggs[55] and Co-workers carried out combustion studies of AP to see the effect of various inorganic additives on it. The additives used were as follows : (a) Oxides of Cu and Cr, (b) Metal Oxides, other than Cu and Cr, (c) other perchlorates and (d) Ammonium salts. The additive concentrations were varied from 2% to 8% by weight. Burning rate measurements were carried out as a function of pressure ($100 < P < 1500$ psi) and initial sample temperature (ambient and 100°C). Following is the summary of their observations :—

1. Of the four "Copper chromite catalysts" tested, the Harshaw Cu 0202 was the most effective.
2. It was speculated from experimental results that Harshaw Cu 0202, CuO, and Cu_2O have their greatest combustion effect in the condensed-phase of the AP.
3. Cu_2O was more effective than CuO in increasing the deflagration rate of AP.
4. $(NH_4)_2Cr_2O_7$, $(NH_4)_2CrO_4$, Cr_2O_3, with the exception of $(NH_4)_2Cr_2O_7$ at room temperature , significantly increased the $\dot{r}$ of AP. $(NH_4)_2CrO_4$ was more effective than $(NH_4)_2Cr_2O_7$.

So far we have discussed the effect of catalyst leading to the sensitization of deflagration rate. Recently Glaskove[9,10] has done detailed studies on the effect of various inhibitors on AP deflagration. The effectiveness goes down as the pressure is increased. The effectiveness factor 'In' is the coefficient of inhibition and is defined as the ratio of the mass burning rate of pure AP to the mass burning rate of AP with inhibitor. She has explained the mechanism for inhibition which is based on the fact that the primary step in AP deflagration is its dissociation to NH_3 and $HClO_4$. She has described three ways for inhibitor action. They are as follows :—

1. By adding readily decomposable salts of ammonia, which can easily give NH_3 in order to shift the equilibrium of the dissociation to the left *e.g.*, NH_4F, $(NH_4)_2BF_4$, $(NH_4)_2SiF_6$, NH_4Cl, NH_4Br, $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ etc.
2. By adding substances which can bind $HClO_4$ or products of its decomposition into less reactive compounds than $HClO_4$ itself or original AP (*e.g.*, Halogenides of different metals.)
3. By adding substances which can inhibit the decomposition of $HClO_4$ (*e.g.*, urea, oxamide, dicyandiamide, hexachloro ethane).

NH_4F was the most effective inhibitor and when 1 % of it is added to AP it deflagrates 3·7 times more slowly than pure AP at 100 atm.

AP Decomposition : The composite propellant contains about 2/3 of its weight as oxidizer which is generally AP. An extensive amount of gasification of the propellant takes place prior to combustion in gas-phase. AP is known to decompose and sublime both under appropriate conditions although it is not clear, precisely, whether the two processes occur simultaneously or can be separated by the choice of experimental conditions. It has yet to be seen whether AP gasification in and outside the propellant is the same or different. From the view point of the direct application, the AP gasification studies at the pressures observed in the actual rocket motors would be more useful. Considering the complexity of the combustion process, the AP sublimation and decomposition under ambient conditions and at low pressures, hopefully, can also throw some light on the process. Numerous aspects of the docomposition and sublimation of AP have been investigated in the past leading to the present understanding of the mechanism involved. The literature on the overall subject is very extensive and has been adequately presented in two reviews[1,2]. In order to describe the salient features of decomposition and sublimation the matter has been classified under following subsections :— (1) decomposition products, (2) decomposition of normal AP, (3) decomposition of catalysed AP, and (4) sublimation. The first sub-section dealing with AP decomposition has been further separated under the heading of various temperature ranges describing different aspects of decomposition.

Decomposition products of AP : Bircumshaw and Newman[56] suggested the following stoichiometric equation which accounts for the principal products.

$$2NH_4\ ClO_4 = N_2O + Cl_2 + 3/2\ O_2 + 4H_2O$$

Heath and Major[57] found the decomposition products to be mainly H_2O, NO, NO_2, O_2 and Cl_2; but Goshgarian and Walton[58] found the major products to be H_2O, NO, O_2, Cl_2, HCl, N_2O and N_2. In both studies, reproductibility of the data is rather poor as judged by inconsistency of mass ratios above that which would be expected from experimental error. Further more, as the AP was decomposed just below the ion source the spectra may include besides products of TD, species derived from the sublimation of AP : NH_3, $HC1O_4$, and the products from secondary reactions involving these two.

Using both natural AP and the isotopically labelled $NH_x\ D_{4-x}\ ClO_4$ and analyzing the decomposition mass spectrometrically Maycock et. al.[59] have shown that principal decomposition products are H_2O, N_2O, Cl_2 and O_2 together with significant amounts of HCl and N_2.

Using a constant volume system which is connected via a molecular leak to a Bendix Model—14 time of flight mass-spectrophotometer, Pai verneker and Maycock[60] made a further quantitative studies of the TD of normal AP together with isotopically labelled AP (obtained by recrystallising normal AP in D_2O). The study showed that the relative pressures of HCl and N_2 were negligible and the major species were H_2O, O_2, Cl_2 and N_2O which are in excellent agreement with the species reported by Bircurshaw and Newman's[56] equation.

Decomposition of normal AP : AP is stable at room temperature, but measurable decomposition starts around 150°C. Around 240°C the phase-transition occurs where orthorhombic structure is converted into cubic structure. Under dynamic heating conditions decomposition of AP completes around 400°C. At temperature above 450°C the TD of AP is very fast. After an induction period it shows a sudden rise in pressure which is often accompanied by a flash of light and rapid burning. This phenomenon is known as thermal explosion.

The literature on the decomposition has been divided into four temperature ranges, two in the orthorhombic form and two in the cubic form. These are discussed below:—

(*a*) *Below 200°C* : The decomposition studies in this region are comparatively much less as compared to high temperature decomposition, primarily because the decomposition is extremely slow. There is no information available on the E estimations in this region. Recently [11], some interesting work has emerged from this laboratory. An indirect way was adopted to estimated E in the temperature range of 75°—150°C. AP was aged for a fixed period of time (12 days) at different temperatures and in this range the aged material was then decomposed 230°C, from the weight loss data, the E value was calculated to be 13±2 Kcal. mole^{-1}. Incidently the same value was also obtained for the propellant ageing process inthe same temperature range. On the basis of the available information in literature on the decomposition products and electrical conduction experiments, it was inferred that proton-transfer takes place during AP decomposition around 150 °C. In the same laboratory recently[61] it has been shown that the charge carrying species at 150°C are the protons. This conclusion gets credence from the fact that the E for the proton transfer is of the order of 15 Kcal. mole^{-1}. Some of the work available in literature presented below also support the fact that proton transfer takes place in the temperature range below 200°C.

(1) Klimenko and Frolov[62] studied TD of AP at 190°C at atmospheric pressure and found that the condensed phase residue contains $HClO_4$.

(2) Boldyrev et. al [63] have studied electrical conductivity through AP crystals below 100°C and found that hydrogen is generated at the cathode. He concluded that the charge carriers were protons.

(3) Keenan and Ohanian[64] have recently studied the electrical conductivity of AP single crystals below 200°C. They concluded that the proton is the conducting ion in the temperature range of 25°C to 100°C.

(4) Hackman, Hesser and Beachall[65] found from mass-spectrometric studies that NH_3 and $HClO_4$ are amongst the primary species formed during decomposition of AP in the temperature range of 80 to 165°C.

(5) Heath and Majer[57] from mass-spectrometric study of the AP decomposition in the temperature range of 110°C to 120°C, found the species like NH_3, $HClO_4$, Cl_2, HCl, nitrogen oxides, O_2, and Cl_2.

(6) Svet lov and Koroban[66] have studied that TD of AP at 150°C by prolonged measurements on a monometer. They have shown that significant amounts of $HClO_4$ are produced.

(7) Recent studies by Kishore et. al.[67] have shown that the preheating of AP at 150°C brings about sensitization in the AP decomposition during certain preheating time and has been explained on the basis of the formation of some acid which perhaps catalyse AP decomposition. The evidence for the acid formation during the preheating has been confirmed from *p*H measurements of aged samples.

(8) Zirkind and Freemen[68] have measured the conductivity of AP in the temperature range of 25-125°C. Their studies have indicated that conductivity to be ionic.

(9) Khairoitdinov et. al.[69] have studied the conductivity of AP and other ammonium salts upto 100°C and found it to be protonic.

(10) Jacobs and Weelam Ng[70–71] studied the conductivity of AP from room temperature to decomposition temperature. The results have been interpreted in terms of the proton transfer from NH_4^+ to H_2O or NH_3 molecule.

(*b*) *200°—250°C* : The decomposition in this region consists of sigmoid curve with an induction period, an acceleratory region and finally a deceleratory region. Many investigators have reported that the decomposition stoped at 30% both by pressure techniques and thermogravimetric techniques. Bircumshaw and Newman, Galway and Jacobs, Jacobs and Kureishy, Raevskii and Manelis, Russell-Jones, Manelis and Rubtsove, Herley and Lavy, Maycock and Pai Verneker all[1, 2] have found E around 30 Kcal. mole^{-1} in this region. While most of the investigators believe the decomposition to be a proton transfer process, Maycock and Pai Verneker[72], however argue that the decomposition proceeds by the initial destruction of NH^+_4 ion interstitials. Assuming Frenkel defect structure in this temperature range it is probable that the NH_4^+ ion is the interstitial based on its smaller size in comparison to ClO^-_4 ion. This process can be expressed chemically as,

$$ClO^-_4 + NH^+_4 \rightarrow ClO^{\cdot}_4 + NH^{\cdot}_4$$

$$NH^{\cdot}_4 \rightarrow NH_3 + H \ (26 \pm 10 \text{ Kcal})$$

The $ClO^{\cdot}_4$ free radical formed in the body of the crystal will be stable owing to the crystalline force field. However, since the decomposition is known to initiate at the surface of the crystal (Bircumshaw and Newman[56]) it is probable that a perchlorate free radical can effectively migrate to the surface by an electron transfer process from ClO_4 ion to the $ClO^{\cdot}_4$ free radical. Break up of the $ClO^{\cdot}_4$ free radical on the surface and subsequent oxidation of the NH_3 will give rise to a decomposition nucleaus which will then grow into the crystal. Decomposition on the inner face of this nucleus will not occur readily because electron-transfer will be more difficult in a disorganized lattice. A very important feature of a mechanism of this type is the requirement for fresh surface for the decomposition to proceed. The formation of Frenkel defects does not lead to production of new fresh surface. The reaction will thus be terminated when all the fresh surface is consumed, with the resultant feature of non-100% decomposition.

(c) *250°—350°C* : In this region 100% decomposition is observed although TG data very clearly show a break in curve at 30 % decomposition level. The decomposition curve for this range is typefied by a short induction period and main reaction being decelerated in nature. Bircum shaw and Newman[56] found E to be 18·5 Kcal. mole^{-1} and they attributed it to the electron-transfer mechanism. Galwey and Jacobs, Jacobs and Kureishy and Russell-Jones all[1,2] have reported E around 30 Kcal mole^{-1} which they associate with proton-transfer process. May cock and Pai Verneker, Inami et.al., Osada and Sakomoto, Raevskii and Manelis, Manelis and Rubtsov all[1,2] have reported E around 20 Kcal mole^{-1}. This value seems to be independent of the techniques employed for decomposition and also whether the experiment is done in vaccum or in an inert atmosphere. Based on the electrical conductivity data, Maycock and Pai Verneker[72] have suggested that the defects structure of AP in this temperature-range is of the Schottky form and hence it is suggested that while defects are beeing consumed the regenerated new surface is also formed simultaneously. Using the decomposition model, the creation of new surface, therefore, would lead to the observed 100% decomposition. The difference in the E for the two regions is possibly due to the different crystal and defect structures. The H atom produced by the destruction of $NH_4^{\cdot}$ free radical could diffuse to the surface and escape or more probably combine with ClO_4 free radical to form $HClO_4$. The $HClO_4$ and HN_3 can then either react chemically or simply sublime. It is obvious that both processes require surface to function properly, with sublimation process dominating under vacuum conditions.

(d) *350°—450°*C: Throughout in this temperature-range the decomposition which exhibits completely deceleratory curve, is associated with extreme fastness and complesion to 100%. Bircumshaw and Phillips[1,2], have reported E 73·4 Kcal. mole^{-1} which they attributed to Cl-O bond dissociation. Galwey and Jacobs, Russell-Jones, Shidloskii et al have reported E around 30 Kcal. mole^{-1} which they associate to proton-transfer process. Kuratoni, Osada and Sakamoto, Maycock and Pai Verneker all[1,2] have reported E around 45 Kcal. mole^{-1}. Maycock and Pai Verneker[72] also calculated the approximate value of the E in this temperature region and found it to be 60 Kcal. mole^{-1} Kishore et. al.[73] recently, using DSC technique found E to be 60 Kcal. more^{-1}. Electrical conductivity measurements by Maycock and Pai Verneker[72] in this temperature region showed that the conduction is electronic and they suggested the rate determining step in the TD is a band to band electronic transition in this temperature range.

Catalysed decomposition of AP : Catalysed thermal decomposition of AP has been studied extensively for the last several years[17,48]. It is surprising that the exact mechanism of catalyst action is not clear even today. TD of AP with several catalysts has been studied very extensively Bricumshaw and Newman[2] proposed the mechanism for action of T. M. O. on AP decomposition. They associated the effectiveness to the ease with which the oxides could provide a bridge in a electron-transfer mechanism.

$$Mn^{4+} + ClO_4^- \rightarrow Mn^{3+} + ClO^{\cdot}_4$$

$$M_n{}^{3+} + NH_4{}^+ \rightarrow Mn^{4+} + NH^{\cdot}_4$$

Particularly extensive studies of the decomposition of catalysed AP have been made by Kuratani and Solymosi et al[2]. Kuratani[2] proposed that only p-type semi-conductors of the T.M.O. were effective in catalysis of the electron-transfer reactions and the oxides of n-type semi-conductors were ineffective, although O_2 was anomolous.

Solymosi et. al[2] studied the decomposition of AP containing metal perchlorates *Ag, Cu, Fe, Cd, Mg, Zn,* and *Li.* He related the effectiveness to the electrical polarizing power of the cations. He considered that the metal ion promote transfer of an electron from the ClO_4^- to NH_4^+ ion.

$$M^{n+} + ClO_4^- \longrightarrow M^{(n-1)+} + ClO_4^{\cdot}$$

$$M^{(n-1)+} + NH_4^+ \longrightarrow M^{n+} + NH_4^{\cdot}$$

The products of AP decomposition in the presence of various catalysts especially with copper chromite have been studied, by Rosser et al[1]. They found the products of decomposition were different from those of pure AP decomposition. He suggested electron-transfer process in presence of catalyst.

$$NH_4^+ + ClO_4^- \longrightarrow NH_4^{\cdot} + ClO_4^{\cdot}$$

followed by decomposition of $NH_4\cdot$ and $ClO_4\cdot$ radicals to gaseous products. Russell-Jones[2] suggested that catalyst promotes proton-transfer reactions. In the process oxidation of $HClO_4$ on the catalyst is followed by the oxidation at NH_3 with the radical so produced.

Most of the transition metal oxides (Cu_2O, CuO, ZnO, Cr_2O_3, MnO_2, Co_2O_3, NiO, Fe_2O_3, $CuCr_2O_4$ etc.) are well-known catalyst for AP decomposition. Kuratani has compared the effects of a number of metal oxides and drawn the following conclusions : (*i*) Cu_2O, CuO and ZnO catalyse both the low-temperature and high temperature reactions: (*ii*) Copper chromite catalyses mainly the high-temperature reaction (*iii*) NiO and Cr_2O_3 promote mainly the low temperature reaction; (*iv*) Al_2O_3, TiO, and V_2O_5 are ineffective in both temperature regions.

Hermoni and Salmon[1,2] found that the presence of oxides of *Mn* (IV), *Co* (II), *Co* (III), *Ni* (*III*) and *Cr* (III) all enabled the low-temperature decomposition to go to completion.

Earlier speculations[1,2] regarding the mechanism of the catalyzed decompositions involved electron transfer, and this has been much used in subsequent work. Copper chromite alters the low-temperature reaction rate only slightly[76] but accelerated the high temperature reaction considerably. CuO is even more effective. This acceleration is associated with a change in the E value from 30 to 48 Kcal/mole. Since the rate of the catalyzed reaction exceeds the sublimation rate at the same pressure, Jacobs and Russell-Jones[74] proposed that $HClO_4$ migrates to the catalyst surface by surface diffusion and there decomposes heterogeneously. Subsequent steps involve the oxidation of NH_3. Support for this mechanism comes from recent work by Boldyreva, Bezrukov and Boldyreva[75] who have shown that NiO, ZnO, Cr_2O_3, Co_3O_4 and CuO can catalyse the decomposition of AP.

Jacobs and Kureishy[1,2] found that Cu_2O oxide exerts a pronounced catalytic effect on the decomposition and ignition of AP. Direct measurements of self heating have confirmed that the explosion is thermal in origin and that it can proceed either by the decomposition of AP which is accelerated by the heat evolved from the oxidation of Cu_2O or that the TD of AP is catalyzed by Cu_2O. Among the perchlorates[76] of the elements of the iron sub-group, cobalt perchlorates has the greatest catalytic effect on the TD of AP. The catalytic effect produced by *Fe* and *Ni* perchlorates is considerably weaken. The influence of the additives is associated with the ease of their transformation during burning into oxides and with the properties of the later.

Korobeinichev et al[77] have made a study of the catalysed TD of $HClO_4$ and NH_4ClO_4 mass-spectrometrically in a flow reactor under non-isothermal conditions. The degree of activity of different catalysts was found to decrease in the following order

$$Co_2O_3 > MnO_2 > CuO > Fe_2O_3 > CuCr_2O_4 > Al_2O_3 > SiO_2$$

Santacesaria et. al[79,80] have investigated the TD of AP in the presence of MnO_2, CuO and Cu_2O, strongly promotes the perchlorate decomposition and modifies the reaction kinetics. CuO and Cu_2O catalyse the decomposition of AP at high temperatures but not at low temperatures. The overall kinetics depends on sublimation. Proton transfer from NH_4^+ to ClO_4^- is believed to be the fundamental reaction step.

Longachev et al[80] have discussed the mechanism of catalytic decomposition of NH_4ClO_4, the catalysts considered were Co_2O_3, MnO_2, CuO, Cr_2O_3, NiO, Cu_2O, V_2O_5 and Fe_2O_3. The important features of the mechanism of catalysts are the contact of the catalyst particles and the diffusion of ClO_4^- anions to the surface of AP.

Ward[81,82] has analysed the data by Keenan and Siegmund on the effect of Cu_2Cl_2 on the decomposition of AP at low temperatures. He has proposed that the mechanism consists of the formation of *Cu*-ammonium complexes subsequent to proton-transfer and these complexes further react with $HClO_4$ or its decomposition products.

Nagaishi et al[85] have investigated the TD of AP in the presence of various metal oxides like Cu_2O, CuO, Cr_2O_2 and V_2O_5. The catalyst activity was in the following order:

$$Cu_2O > CuO\ Cr_2O_3 > V_2O_5$$

The rate determining step in CuO and Cr_2O_3 catalysts seem to be the TD of ClO_4^- via the rupture of the *Cl-O* bond.

Kishore et al[84] studied the TD of powdered AP catalysed by MnO_2 in the low concentration ranges of catalysts. They found that MnO_2 sensitises the TD of AP and the E for catalysed AP was to be 30 Kcal. mole^{-1} throughout the low and high temperature regions whereas uncatalysed AP gives two E, 20 Kcal. mole^{-1} in the low temperature region (280-320°C) and 60 Kcal. mole^{-1} in the high temperatures region (350-390°C). They attributed this behaviour of catalysed AP on the basis of an electron-transfer process.

Kishore and Sunitha[85] studied the mechanism for the action of T.M.O. (Cr_2O_3, Fe_2O_3, Mn_2O_3, CaO, Cu_2O) on the r of PS/AP propellant. They found that these oxides promote electron-transfer process during the propellant decomposition which also effects the r in the similar fashion. They supported their mechanism on the basis of the linear dependence between the degree of increase in r with redox potentials of the oxides and also with the heats of reaction associated with the electron-transfer process.

Kishore et al[86] studied the effect of T.M.O. (Fe_2O_3, Co_2O_3 and MnO_2) catalyst concentration on the r rate of composite solid propellant. They found that TD of the AP containing these oxides and propellant r show a saturating effect at 1% of the catalyst. The behaviour of the AP decomposition and propellant behaviour was similar.

So far we have discussed the effect of catalyst leading to the sensitization of AP decomposition. Mayer and Co-worker[87], by using DTA technique investigated the possible ways which could suppress the low-temperature exotherm of AP decomposition. The first exotherm was eliminated by controlled heating of the AP for several minutes at 270°-390°C. The inhibitors used were ammonium salts of complex halogen anions (e. g. NH_4PF_6, NH_4BF_4, $(NH_4)_2TiF_6$, $(NH_4)_2SiF_6$, and NH_4SO_3F). The most effective inhibitor was NH_4PF_6. They observed that the temperature at which first exotherm in AP decomposition occured could be raised to 85°C by adding 1·5% NH_4PF_6.

Munson and Reed[88] found spray-drying $(NH_4)_2HPO_4$ and $NH_4H_2PO_4$ on to AP was effective in shifting the low-temperature DTA exotherm to higher temperature. Pellet and Cofer[89-91] in essential agreement with others found that AP co-crystallized with $(NH_4)_2HPO_4$ had retarded low-temperature decomposition of AP. This was attributed to a complexion between PO_4^{3-} co-crystallized with AP substantially reduced the rate of low temperature decomposition while the high temperature decomposition was uneffected. Schmidt[92], like Pellet, attributed this effect due to the complexing of the PO_4^{3-} with $HClO_4$. Boldyrev[93] also found that of temperature 240°C $(NH_4)_2HPO_4$ retards AP decomposition.

Sublimation of AP

Sublimation of AP was first reported by Dode[1,2] and quantitative measurements on the sublimation of AP were first done by Bircumshaw and Phillips[1,2]. Because AP decomposition is a competing process, they first decomposed 30% of the AP at low temperatures and then studied the rate of sublimation in vacuum from 260°C to 320°C by weight loss technique. The E is reported to be 21·5 ± 2·8 Kcal mole^{-1}. They advocated proton-transfer as the rate determining step in the sublimation process. Later Inami et al[1,2] using the transpiration method studied the dissociation pressure of AP and concluded that AP undergoes congruent dissociative sublimation by the process.

$$NH_4ClO_4 \rightleftharpoons NH_3\,(g) + HClO_4\,(g)$$

with a heat of dissociation of 58 ± 2 Kcal/mole. These data show a very reasonable analogy to the sublimation process in ammonium halides. Mack, Tompa and Wilmot[1,2] identified NH_3 and $HClO_4$ as the products of sublimation. Chaiken et al[1,2] experimentally determined the Arrhenius rate parameters for the sublimation of ammonium halides and noted that the E increases linearly with increasing molecular weight and is approximately one-third the heat of sublimation. Similarly from the above data the E for the sublimation of AP is one-third of its heat of dissociation and is proportional to its molecular weight when compared with the ammonium halides.

However, Jacobs and Russell-Jones[94] have recently remeasured the E for the sublimation of AP, using the same approach as that of Bircumshaw and Phillips[1,2] and found the value of the E to be 30 Kcal/mole. They analysed their vacuum sublimation data using the contracting sphere relation. By overlooking the kinetics of the process which lead to the proton-transfer they argued that the value of their E was correct since it was one-half of the heat of sublimation. They discarded the value of Bircumshaw and Phillips[1,2] of 21 Kcal/mole based on the fact that it was derived from a limited study. Guirao and Williams[95] have, since then, discussed theoretically various models for the sublimation mechanism of pure AP and as a result have suggested that the results of low-temperature decomposition. The results of Jacobs and Russell-Jones[94] also make the analogy between the sublimation parameters of AP and of other ammonium halides invalid. To help clarify this discrepancy, Pai Verneker et al[96] studied the TD as well as the sublimation of AP simultaneously from 200 to 380°C using the thermobarogravimetric (TBGA) technique[97]. This has been supplemented by a calculation of the E based on the Schultz-Dekker[98] linear theory for sublimation. They found that AP primarily sublimes below 20 torr of pressure and above it sublimation is accompanied by decomposition. At most ambient pressure very little sublimation is observed.

Recently, Kishore and Pai Verneker[99] analysed that E and enthalpy for the sublimation of AP together with other ammonium salts and found that in all cases E is one-third of the enthalpy of sublimation.

Pai Verneker and Co-workers[100] have shown that pre-compressed AP sublime faster than the uncompressed one, Ca^{2+}, Cl^-, SO_4^{2-} and PO_4^{3-} ion doped AP sublime slowly compared to undoped one, and the preheated AP sublimation gets desensitized. They have suggested that in pre-compressed AP gross-imperfection plays a role during sublimation, whereas in doped and preheated AP it is the strain which controls the sublimation process.

Pai Verneker et al[101] compared the pre-treatment on AP like, doping, preheating, pre-compression and changing the particle size on TD and sublimation of AP. They found that while pre-compression and particle size show a similar behaviour both in decomposition and sublimation, the pretreatment like doping and preheating show a significant difference in the two processes. They concluded on the basis of divergence in the behaviour of sublimation and decomposition of preheated AP, that decomposition does not involves proton-transfer as the rate controlling step, since it is well established that sublimation of AP involve proton-transfer as the rate determining step.

Summary of the AP decomposition and sublimation mechanism

Looking at the overall picture, it may be said that, although the AP decomposition has been a subject of an intensive investigation for last 20 years, it has not solved many of the interesting problems, one amongst them, being the low temperature decomposition. From the view point of the use of AP in propellants formulation the decomposition mechanism can be considered to involve two different schools of thought. One school believes that the rate controlling step in the decomposition is the proton-transfer,

$$NH_4^+ \cdot ClO_4^- \longrightarrow NH_3 + HClO_4$$

Whereas the other school believes in traditional solidstate process, and adequate electron-transfer mechanism.

$$NH_4^+ \cdot ClO_4^- \longrightarrow NH_4^{\cdot} + ClO_4^{\cdot}$$

Recent experiments on ionic conductivity of AP (pure and doped) do point in favour of diffusion[103,104]. However, more experimental evidence is desirable to unequivocally decide in favour of one mechanism. As regards the mechanism of sublimation it is almost accepted that the sublimation of AP involves proton-transfer process[2,94,96,105]. The mechanism of sublimation and decomposition are summarized in Table 2.

TABLE 2

MODEL FOR SUBLIMATION AND TD OF AP

1. *Proton-transfer model for sublimation and TD (Ref. 2)*

(*a*) Sublimation

$$\begin{tikzcd}
NH_4^+ & + & ClO_4^- \arrow[r, shift left] \arrow[r, leftarrow, shift right] & NH_3\,(g) \arrow[dd, shift left] \arrow[dd, leftarrow, shift right] & + & HClO_4\,(g) \arrow[dd, shift left] \arrow[dd, leftarrow, shift right] \\
\text{Sublimate} & & & & & \\
NHClO_4(s) & & {} \arrow[r, shift left] \arrow[r, leftarrow, shift right] & NH_3\,(g) & + & HClO_4\,(g)
\end{tikzcd}$$

E = 30 Kcal/mole

(*b*) Decomposition

$$\begin{tikzcd}
HN_4^+ & + & ClO_4^- \arrow[r] & NH_3\,(g) \arrow[d] & + & HClO_4\,(g) \arrow[d] \arrow[r] & \text{Products} \\
 & & & NH_3\,(g) & + & HClO_4\,(g) \arrow[r] & \text{Products.}
\end{tikzcd}$$

E = 30 Kcal/mole.

Essential feature of proton-transfer model : —

(*i*) Only one value of E for decomposition, throughout the temperature range 200–260°C.

(*ii*) E for TD and sublimation are same supporting that same mechanism hold good.

2. *Proton-transfer/ionic diffusion/electron-transfer model for* (*Ref. 11, 72, 73, 106*).

Essential features :—

(*i*) Four values of E for TD of AP

$$E = \frac{\text{below } 200°\text{C}}{13 \text{ Kcal. mole}^{-1}}, \frac{200°\text{–}250°\text{C}}{30 \text{ Kcal. mole}^{-1}}, \frac{250°\text{–}350°\text{C}}{20 \text{ Kcal. mole}^{-1}}, \frac{350°\text{–}450°\text{C}}{60 \text{ Kcal. mole}^{-1}}$$

(*ii*) Activation energies for TD and sublimation are different, sublimation (200°–380°C), $E = 20$ Kcal. mole^{-1} (below 20 torr).

Model for decomposition :—

$$NH_4ClO_4 \longrightarrow NH_4^+ + ClO_4^- \longrightarrow NH_4^{\cdot} + ClO_4^{\cdot} \longrightarrow \text{Products}$$

Steps involved :—

(*i*) At very low temperatures (below 200°C) NH_3 and $HClO_4$ are formed.

(*ii*) Migration of NH_3 to a preferential site for decomposition (rate determining step in low temperature (200–350°C) range decomposition).

(*iii*) Electron-transfer from ClO_4^- to NH_4^+ (range determining step in high temperature (above 350°C) range decomposition).

(*iv*) Reaction between ClO_4 and NH_4 to give the products of decomposition.

The results on the studies on the effect of pre-treatment on AP decomposition and sublimation[190—108] have revealed that the sublimation and TD processes follow different mechanisms. That the proton-transfer is the rate controlling process during the sublimation is well established. Hence, it suggests that the TD does not involve proton-transfer process.

NOMENCLATURE

AP=Ammonium perchlorate

APP=Atactic polypropylene.

CMDB=Composite modified double-base.

CPIA=Chemical Propulsion Information Agency, the Johns Hopkins University, Applied Physics Laboratory, Silver Spring, Maryland, USA.

CTPB=Carboxy terminated polybutadiene.

DAA=Diphenylamine.

E=Activation energy.

ERDE=Explosives Research and Development, Waltham Abbey, Essex, England.

HTPB=Hydroxy terminated polybutadiene.

LPL=Low pressure deflagration limit.

NC=Nitrocellulose.

NG=Nitroglycerine.

PB=Polybutadiene.

PBAA=Copolymer of butadiene with acrylic acid.

PBAN=Terepolymer of butadiene with acrylic acid and acrylonitrile.

PE=polyester.

PMMA=Poly (methyl methocrylate) .

PS=Polystyrene.

PU=Polyurethane.

PVC=Poly vinyl chloride.

r=Burning rate.

RPE=Rocket Propulsion Establishment, Westcott Buckinghamshire, England.

Tg=Glass-translation temperature.

TD=Thermal decomposition.

T.M.O.=Transition metal oxide.

UPL=Upper pressure deflagration limit.

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