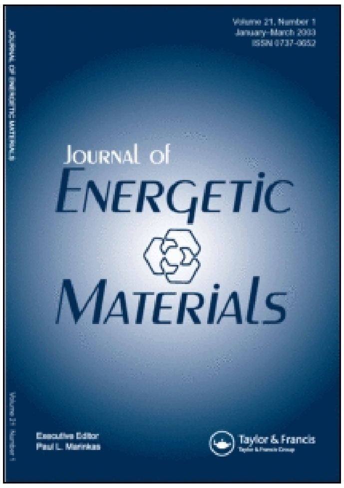

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

Catalytic decomposition of ammonium perchlorate a survey

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To cite this Article Ramamurthy, S. and Shrotri, P. G.(1996) 'Catalytic decomposition of ammonium perchlorate a survey', Journal of Energetic Materials, 14: 2, 97 — 126

To link to this Article: DOI: 10.1080/07370659608216060

URL: http://dx.doi.org/10.1080/07370659608216060

CATALYTIC DECOMPOSITION OF AMMONIUM PERCHLORATE A SURVEY.

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ABSTRACT

This paper reviews the role of additives in the combustion process of ammonium perchlorate.These additives are found to influence the low temperature decomposition of AP,its ignition temperature and burning rate. Transition metal oxides and various other compounds like chromates,halides, carbonates and perchlorates are well known decomposition catalysts. Admixture of these compounds is found to change the pattern and products of decomposition. The mechanism of decomposition is explained on activation energy obtained from thermal data.The activation energy of ammonium perchlorate is attributed to transfer of electron from perchlorate ion to ammonium ion and the role of catalyst is to accelerate this proccess. A complex is formed with metal ion ClO_4^- and NH_4^+ radical which stabilizes the electron transfer process.

INTRODUCTION

Ammonium perchlorate (AP) is found to play a key role in the combustion of composite propellants. It has been observed that the decomposition and burning properties of AP can be largely improved by using various catalysts.

Journal of Energetic Materials Vol. 14, 97-126 (1996)
Published in 1995 by Dowden, Brodman & Devine, Inc.

Transition metal oxides like Fe_2O_3, CuO, MnO_2 and Cr_2O_4 etc. form a popular group of catalysts which affect the decomposition of pure AP and are used as burning rate modifiers of composite solid propellants. Though a few reviews (1,2,3,4), are published the exact mechanism of their action is still not known. Much scattered information is available about propellant decomposition, oxidizer decomposition and sandwich and condensed mixture combustion. The purpose of this review is to bring about comprehensive coverage of the information available. An attempt is also made to understand the mechanism underlying the decomposition taking into account various theories and hypotheses put forth by various authors. The review covers most of the literature available upto Dec.1993.

THERMAL BEHAVIOUR OF AP

Pure AP (fig.1) a white crystalline solid is stable at room temperature but measurable decomposition starts around 150°C. The initial endothermic peak around 240° C is the transition peak where crystallographic modification of AP from orthorhombic to cubic form occurs. The process is accompanied by a simultaneous dissociative sublimation and exothermic decomposition. At about 260°C slight inflection on the TG curve may be attributed to the different decomposition kinetics of the cubic form. The thermogram shows a low temperature exotherm (LTE) at 327°C. which corresponds to 30% decomposition. The residue left is identical with the starting material, although the plot of fractional decomposition (α) against time is sigmoidal in nature like many other solid phase decompositions, where the reaction goes to completion.The process is autocatalytic and the decomposition is complete.The high temperaturee exotherm (HTE) occurs at about 400°C.As the temperature increases[5] deflagration or rapid combustion occurs at 450°C.

In the works of various authors only slight difference is found in endothermic temperature. The differences are ,however,in the exothermic temperatures. The parameters like particle size, heating rate,amount of the sample etc affect the DTA curves. The temperatures at which the peaks appear vary with the gas atmosphere also. For example,the DTA curve in vacuo, is different because beyond 290° C a broad but deep endothermic band indicates sublimation. The DTA characteristics in nitrogen do not differ significantly from those in air,but in ammonia, the first exothermic effect is suppressed and the combustion peak at 420°C is significantly enhanced.

KINETICS[6]

The thermal reactions of AP are usually complicated. In low temperature reaction the α - t curve (α = fraction decomposed) obeys the Avrami-Erofeev.equation :

$$1 - (1 - \alpha)^{1/n} = kt$$

wherein n = 3 in vacuum tending to 2 as the pressure increases. Many of the published values are in the range of

30 to 50 K cal / mole.

Satisfactory results are obtained for both accelaratory and decelaratory stages by using Prout- Tompkin's equation

$$\log \frac{\alpha}{1-\alpha} = kt + c$$

Studies on high temperature thermal decomposition of AP in the range 380 - 450 was done by Bircumshaw and Newmann at a pressure range of 120 to 140 torr to reduce sublimation. The equation was contracting cube equation and the activation energy determined was 38.8 K Cal/ mole.

Along with decomposition, AP undergoes sublimation. Bircumshaw[7] and Newmann showed that AP decomposes to limited. extent (30%) below 300°C. If the temperature is raised sublimation of this residue occurs. The activation energy at this rate of sublimation is approximately 21 K Cal/mole.

Sublimation rates under vacuo when measured showed E to be 30.K .Cal /mole. At higher pressure the rate tends to be towards constant value but as pressure is decreased there is a decrease in the rate constants. The evaporation coefficient varies from 4 x 10 for sublimation in vacuo to about 5 x 10 at 1 atm. pressure.

MECHANISM[2]

Mechanism of decomposition of AP is explained in the following steps;

1) Transfer of electrons from ClO_4^- to NH_4^+ in low temperature reaction.

2) Transfer of protons from NH_4 + to ClO_4 - in sublimation .

3) Decomposition of ClO_4^- due to break down of Cl-O bond in high temperature reaction.

Low Temperature Thermal Decomposition of AP:

The proposed mechanism is electron transfer from a ClO_4 anion to an interstitial cation (NH_4) which results in adsorbed ammonia and $HClO_4$ radical on the surface of AP.

Since the reaction is catalyzed by $HClO_4$ and retarded by NH_3 it is proposed that bimolecular reaction of adsorbed perchloric acid molecules is

$2HClO_4$ ---> H_2O + ClO_3 +ClO which further splits into O atoms and ClO radicals.

High Temperature Thermal Decomposition of AP

The reaction is decelaratory throughout without any induction period and results in the complete decomposition of the salt. If the oxidation of NH_3 proceeds with less than 100 efficiency through decomposition of perchloric acid then NH_3 will accumulate on the surface thus suppressing the proton transfer reaction where it ceases completely, .As the temperature is raised desorption of NH_3 occurs, dissociation recommences and both NH_3 and $HClO_4$ are desorbed into the gas phase rather than on the surface.

Sublimation

Sublimation occurs along with decomposition. The gaseous products formed due to sublimation are perchloric acid and ammonia.

Recent development in AP[8] decomposition mechanism discusses the formation of nitrosyl perchlorate as an intermediate product.The important characteristic of this new intermediate is that the stability of perchlorate ion is reduced by forming a covalent bond NO_2 -O -ClO_3 .

Qualitative kinetic comparison showed that the reaction rate agreed with expectations for a process controlled by small amount of NO_2ClO_4 determined analitically to be present in partially decomposed AP. NH_3 oxidation leads to regeneration of NO_2ClO_4 and this perpetuates decomposition.

GASES EVOLVED DURING DECOMPOSITION [9]

Oxygen and oxides of nitrogen are noticed after transition. Dode identified chlorine, chlorine dioxide nitrogen, water, oxygen ,nitrous oxide, nitric oxide with chlorine and oxygen (nitrosyl chloride) nitrogen trioxide and nitrogen dioxide etc.below 300°.The distribution of nitrogen between elemental nitrogen ,nitrous oxide and nitric oxide is temperature dependent.Below 300 nitrous oxide predominates but above this it is nitric oxide.In addition to HCl perchloric acid is also present . Substantial redistribution of chlorine among the products was occurring in different temperarature regimes.At low temperature chlorine appears as Cl_2 and ClO_2 whereas at high temperature (380 -450) there is an equal distribution of chlorine between the acids and Cl_2 and ClO_2 .

Spectral analyses [10] are made at lower temperature and pressure. By mass spectrometer at 80° $-ClO$, ClO_2 ,ClO_3 and $HClO_4$ are detected . At 115° HCl is prominent along with N_2O ,NO, and Cl_2 .At 135° HNO, ClO, ClO_2 are abundant $HClO_3$ and $HClO_4$ also appear which are abundant at165° .Traces of NH_2 and NH_4 also appear. Oxygen is mainly due to dissos-iative sublimation .

CATALYTIC ACTIVITY OF ADDITIVES ON PURE AP

The characteristic features of thermal stability of AP is extremely sensitive to additives. Catalysts are found to influence the reactions both in accelaratory and decelaratory phases.Rate of burning is substantially increased or decreased by them which result in profound modification in kinetic characteristics and the products of reaction. Sometimes catalytic reactions occur without concurrent sublimation .Transition metal oxides are the main catalytic agents.Other than oxides, chromates halides , carbonates, perchlorates ect. also modify AP decomposition behavior.

OXIDES

Iron Oxide[11]

Fe_2O_3 reduces the induction period to zero and increases both reaction rate and extent of pure AP decomposition. In the presence of little oxide above 240 °C 25-28% conversion of AP is at the same rate as in the case of pure AP.1:1 molar ratio of Fe_2O_3 causes longer decomposition and doubles the reaction rate . The $\alpha - t$

curves are autocatalytic and the t-max is maximum for powdered mixtures. The decomposition is found to proceed upto 90 to 95%.

Kinetics is determined by Prout Tompkin and Avrami - Erofeev's equation. E was found to be 32& 30.5 K Cal/mole for accelaratory and decelaratory periods respectively. At the same temperature Sidoviskii found it to be 41.0 K Cals/mole. By DSC it is 48 K Cal/mole at 300 to 335° C.

Explosion of AP in the presence of Fe_2O_3 occured at a lower temperature. The minimum ignition temperature of AP decreased gradually with the increase of catalyst. At the lowest temperature below 300° C the 1:1 molar mixture explodes. Deflagration rate is decreased by Fe_2O_3 below that of pure AP at low pressures and promoted at high pressures.

Manganese Dioxide:[12]

The kinetic decomposition of mixtures of $AP+MnO_2$ compressed to a rigid pellet was studied by Jacobs and Galwey in the temperature range 137 -212° C. Sublimation does not occur, the reaction occurs in two stages ,the first stage is linear, the kinetics fits in the equation p = mkt. In the second stage E value was about 30 to 33 K Cal /mole .Other oxides of manganese are unstable.

The second stage of the reaction is a normal uncatalysed decomposition of MnO_2. The ceasation of reaction before the decomposition of the salt is complete, indicates that contact between salt and catalyst is lost at an early stage corresponding to about 4% of the salt. This view is supported by the kinetic results. The occurrence of linear reaction period in pellets of high AP concentration indicates that interfacial area remains constant.In loose mixture catalyzed reaction persists to much later stage as contact is renewed between the particles.

The stabilization of the reaction is by electron transfer from perchlorate ion to the surface $(Mn^{3+}ClO^{4-}NH^{4\ +})$. The gases evolved are N_2, ClO_2 and H_2O.

Copper(1) and Copper (11) Oxides[13]

Cu_2O and CuO both increase the decomposition of AP below 240°C.In the presence of Copper(1) oxide AP explodes at 248° C. The two important factors involved are the oxidation of Copper (1) oxide and the catalytic effect of Copper (11) oxide that is formed.

Copper (1) oxide is also found to influence the induction period (τ). Hermoni and Salmon studied the effect at 270° C under 250mm of N pressure. From 0 .5 to 8% τ increases and from 8 to 20% CuO remains sensibly constant. Then it falls sharply to half its previous value and decreases slowly. With increase in CuO. the reaction is supposed to take place in three stages. The first stage is the catalysed decomposition of AP caused by contact with Cu_2O.The reaction with no (τ) does not propagate far into the salt particles and soon ceases.After a total induction period of a few minutes AP decomposes slowly .Oxygen resulted from this and the initial interface reaction is highly exothermic.The decomposition of AP is accelerated and the self heating due to further oxidation and from the exothermicity of the perchlorate decomposition may result in ignition.

The oxides are found to increase the LPL. Two processes are supposed to occur ,increase in the radiation heat loss from the surface and increase in the radiative feedback to the surface. These catalysts are also found to accelerate AP deflagration via their action in the condensed phase.

The catalytic effect of Copper (11) oxide can be observed even with 5% of CuO. The equations fitting the kinetic data are Avrami - Erofeev and Prout - Tompkins and the E value is between 29 to 33 K Cal/ mole, above 240°C, E is 48 to 53 K Cal/ mole which may be due to change in the mechanism.

As CuO is a semi conductor,its electrical conductivity is changed by doping 1% Li_2O_3; doped copper oxide decreased the decomposition of AP much below ,while Cr_2O_3 doped CuO increased the inductive period. The explosion temperature of AP is decreased in the first case and is increased in the second case.

Magnesium Oxide [14,a,b.]

Magnesium oxide is both accelerating and inhibiting oxide, depending upon the amount of oxide used .With little MgO, accelatating effect is observed , whereas excess oxide hinders the decomposition process.The rate decomposition is maximum with 2:1 AP - MgO mixture in the range 200 - 235° and least at 206-235° C.Above 300° even a small amount of oxide gives inhibition effect. After the induction period the oxide acts as accelerating catalyst and this effect depends on the amount of oxide used.Even the explosion temperature depends on MgO content ,being 270° C for 100:1 ratio. and 336° for 25: 1 ratio mixture. The mechanism suggested is the formation of Mg-perchlorate which further activates the reaction rate.

Cobolt Oxide[14]

Hermoni.et al[14] obtained E value for AP catalyzed with cobalt oxide as 33K Cal /mole at 170 -200° C and 42 K Cal/ mole at 210-230° C. But Sidoviskii[20] obtained 38.3 K Cal / mole. The change in the E value may be due to change in the mechanism .In the presence of this oxide AP explodes at 241°

Nickel Oxide[14].

Harmoni found that if powder mixture of AP+NiO is used AP decomposed completely. E value is found to be 33K Cals/mole at 210-240° C using contracting cube equation. Sidoviskii's results were also almost the same.

Like CuO, NiO affects the decomposition temperature of AP due to its electrical properties . NiO doped with lithium oxide acts as a better catalyst.But chromium oxide doped NiO decreases the catalytic effect. With these doped oxides E value was found to be 30-35 K Cals / mole. The decrease in the catalytic effect may be due to the fact that the doped oxides modify the defect structure and the electronic structure of NiO .

<u>Cadmium Oxide</u>.[15]

Small amount of catalyst 10% and 16% molar ratios shows catalytic effect. At 200-240° C 28 k Cals/mole of activation energy is obtained. With large amount of catalyst the induction period is long.

CdO reduces the induction temperature by about 130° C but the induction period is long approx. 17 minutes. Investigations prove that presence of small cadmium particles in CdO is responsible for lowering of ignition temperature. CdO is found to form perchlorate salts with AP.

<u>Aluminium Oxide</u>.[16]

It is found to be totally inactive.

<u>Calcium Oxide</u>.[17]

From the DTA data it is found that the first exotherm of AP falls and its flash point also falls down progressively proving the catalytic effect of CaO.

The effectiveness of CaO was estimated by reference to the inhibition factor 'In', equal to the ratio of pure AP to that of AP + CaO .At 50-100 atm. pressure the inhibition factor is increased with CaO content from .1 to 3%. Burning rate with 3% CaO and 50 atm is 4.3 times less than that of pure AP. 1 to1.5 % CaO has maximum inhibition effect, where the pressure interval is 100- 250 atm.The weakening of inhibition effect continues upto 300 atm. Then CaO accelerates the combustion of AP.

The mechanism is that the inhibition of the combustion process is due to the formation of less reactive calcium perchlorate.The resulting NH_3 is removed from the reaction zone and thus does not exert a retarding effect. In combustion , however , the excess ammonia formed is not removed and the process is retardation.Exess ammonia formed as a result of combustion with $HClO_4$ shifts the dissociation to the left.

Zinc Oxide[18]

With ZnO decomposition of AP occurred at 240°C to the extent of 75 to 85 %.The reaction rate does not depend upon the amount of ZnO and considerable effect occurred even in the presence of 1 % oxide. Contracting cube equation was found to be the best fit and the E value was found to be 32 K Cals/mole.ZnO belongs to n-type semi- conductors and its electrical properties can be effectively influenced by doping with foreign ions of different valencies. The rate of reaction was accelerated by increasing its conductivity with 1% Al_2O_3 and is lowered by decreasing the conductivity with 1% lithium oxide. Doping also largely increased the induction period of AP. Catalyzed decomposition of AP is best followed at 240°C with 1%ZnO.After the induction period the substance exploded. With increased amount of ZnO instead of explosion degeneration of AP occured.

The residue obtained after decomposition of AP was found to be Zn perchlorate which forms an eutectic of lower M.P with the remaining AP.

Titanium oxide and Chromium oxide[14,11a]

Pure titanium oxide is practically inactive. However, doped titanium oxide with chromium oxide decreased ignition temperature of AP by 150°. Pure AP doped with Cr_2O_3 gave an E value of 26.7 to37.7 KCals/mole at 210-230° and 250-275° respectively.But when doped with tin oxide,its catalytic charecter is improved.From detailed investigation it is found that chromium ions are oxidized to higher states which were stabilized by tin (1v) oxide lattices.

Yittrium Oxide.[19]

The decomposition temperature of AP is found to decrease with Y_2O_3 concentration,attains minimum at about 3.5% and again increases. Prout - Tompkin and contracting - cube equation (n = 3) were found to fit the TG data. E value was found to be approximately 106 and 214 K Joules per mole at accelaratory and decelaratory periods respectively. Catalitic activity which is the ratio of the rate of decomposition of catalyzed AP to the rate of decom - position of uncatalysed AP is found to be 26.16% at 240° C . Gases evolved during decomposition , identified by IR technique are N_2O at approximately 230° C and NO above 300° C.

Lanthanum oxide and its analogs.[20]

Lanthanum oxide and its analogs are also found to be (Nyodimium and Cerium oxides) useful as catalysts. 3.5% of the catalyst was found to be of optimum concentration which brings about maximum decrease in the ignition temperature of AP. Prout Tompkin and contracting cube equations are found to fit isothermal TG data. Rate constants are found to increase with temperature in both accelaratory and decelaratory periods.Energy of activation is approximately 42 K Cals/ mole with Lanthanum and Niodymium oxides and with Cerium dioxide it is approximately 32K Cals/ mole. The variation in the activation energy may be due to change in the mechanism.The main gases evolved during decomposition of catalysed AP is N_2O at 300°C and NO at 350°C

OTHER SALTS

Even the other salts like chlorides , chromates perchlorates ect. catalyze the decomposition of AP.

Chlorides.[20,21]

1. Calcium chloride: By adding 25-30% of calcium chloride a gradual reduction is observed in the frequency of explosion to zero. Sharp reduction in flash point is observed with 15% $CaCl_2$ .The low temperature decomposition of AP is at 290° C and high temperature decomposition is at 410°C. $CaCl_2$ has an effect not only on the second decomposition temperature but it also changes the nature of the DTA curve. With 25 to 40% calcium chloride two stages are there at 320°C and above 40% calcium chloride has no effect.

2. Copper Chloride.

Cu_2Cl_2 catalyses both high and low temperature reactions. It accelerates the low temperature decomposition of AP to such an extent that there is no second stage. AP also deflagrates even at 1 atm with 3 % Cu_2Cl_2 and $CuCl_2$.

3. Ferric chloride.

$FeCl_3$ catalyses the low temperature decomposition so that there is no second stage.

4. Magnesium chloride Sodium chloride and Potassium chloride;

They reduce high temperature decomposition of pure AP.

5. $MnCl_2$ and $CoCl_2$.

They bring down the decomposition temperature of AP to 210 - 220°C with much reduced induction period.

6. $NiCl_2$ and $CrCl_3$

They affect the decomposition temperature of AP only above 240° C .

Chromates and Chromites.[22]

Copper chromate: alters low temperature decomposition reaction slightly but accelerates the high temperature reactions considerably with or without carbon. It is found to decrease LPL in small proportion but increases it if large quantity is used. α - t curve is decelaratory and contracting square equation is found to be suitable. Excess catalyst stops the autocatalytic nature of AP. E value is found to be around 42 KC /mole with 1 : 1 molar ratio. AP explodes at about 265°C deflagration is effected as copper chromite increases the lower pressure limit.

Carbonates[23,24] :

Carbonates are another class of compounds which affect the decomposition of AP . Thermal decomposition of AP is increased in the presence of basic copper carbonate and chromium carbonate. Rate constants are increased in accelaratory and decelaratory periods, E is also higher than that for AP. Carbonates get converted to oxides and hence the oxides and not the carbonates are the real cause of catalysis.

Carbonates of alkaline earth metals like $SrCO_3$ and $BaCO_3$ as well as Li_2CO_3 also remarkably change the AP decomposition temperature and hence are used as catalyst in AP based composite propellants.

Fluorides[25]:

The thermal decomposition of AP is catalyzed by metal fluorides.The effect is due to the formation of metal ammonia complexes which facilitate proton transfer step in the decomposition of AP. The effect is transition metal> alkaline earths > alkali metals.

With metal fluorides the decomposition takes place in one step at 280-310°C. The isotherm obtained at 230° with metal fluorides and AP shows an induction period of about 50 min. The extent of AP decomposition with metal fluorides in 250 min is CoF_2 ,MnF_2 = 90%, ZnF_2- 82% CuF_2 -43%

NiF_2- 30% and pure AP 25%. ZnF_2 shows an anomalous behaviour. The metal fluorides react with AP on heating and give NH_4F and HCl. CuF_2 reacts with AP and gives $CuCl_2$. Similarly MnO_2, Co_2O_3 and NiO are identified. Due to strong affinity of fluoride ions on proton HF is formed which suppresses the formation of $HClO_4$ leading to delay in the ignition temperature. Copper and nickel fluorides act as good catalyst above 240° C. But because of large induction period use ofmetal fluorides is minimized.

<u>Perchlorates</u>[26]

Perchlorates of metals also catalyze AP decomposition.

Silver Perchlorate : enhances AP decomposition below 240° C . The action is autocatalytic and stops at 40-45% decomposition and the E value is found to be nearly 30 K Cals / mole.

Copper and Iron perchlorates : cause explosion even when one mole is added.

Zinc Cadmium and Magnesium perchlorate : have effect at even 200 - 240° C and the decomposition proceeds to 100 %. E value is approximately 30 K Cals / mole. With cadmium and magnesium perchlorate they decrease the ignition temperature by about 200° C. Explosion is found to occur at 250° C.

Lithium perchlorate : causes 90 -95 % decomposition of AP. Temperature of explosion is 320 -340° C. Excess amount of lithium perchlorate causes explosion at 290° C, with a long induction period of 2 to 3hrs.

Alkyl ammonium perchlorate[26] :

Pai Varnikar added methyl ammonium perchlorate and trimethyl ammonium perchlorate and studied the decomposition process of AP by DTA.The mixture ignites at about 300°C at slow heating rate in contrast to pure AP which decomposes in two steps.. At low concentration of the alkyl perchlorate there is an enhancement in the intensity of the first exotherm , and reduction in the second until at critical concentration the whole mixture ignites at 290° C showing a single exotherm.With trimethyl ammonium perchlorate the terminal exotherm of pure AP is shifted to a higher temperature. With tetramethyl AP because of its simple and uncomplicated decomposition behaviour there is not much transition in the decomposition range of AP.

Other salts[27] :

Salts of ammonium halogeneids and deoxidents are inhibitors which decelerate the combustion process.

The coefficient Inhibition - 'In' = Rm =

$$\frac{(\text{Ratio of mass burning rate of AP})}{(\text{Ratio of mass burning rate of AP+additives.})}$$

is used to calculate the inhibition effect.The effect of burning inhibitors decreases with Rm and LPL. The influence of different metal introduced into the salt of of hydrohaloide acids also influence the inhibition effecton AP. For example boron in the molecule of the salt strongly reduces the inhibition effect. Similarly 5% NH_4F, $(NH_4)_2SiF_6$ also suppresses the first exothermic reaction. Ammonium - diphosphate ,ammonium fluoride are also effective inhibitors. Halogenoids of lead , cadmium and zinc are also good inhibitors. Stabilisers like diphenyl amine are effective in inhibiting AP deflagration.

Amines[27]. :

Amines like urea , oxamides,dicyandiamide act as deoxidents.As the additive content is increased LPL also increases. Aromatic amines are less effective burning inhibitors, because aromatic amines are more easily oxidized by $HClO_4$. Water , hexachloroethane (C_2Cl_6) are effective inhibitor of $HClO_4$

Metals:

1. Aluminium particles[28] :

For the ignition of Al, the temperature of the oxidizing agent must be more than alumina. Surface oxidation is inhibited by larger particle size.The combustion process of AP is enhanced if Mg-Al alloy or Mg- Li alloy is added.

AP is considered to decompose only at hot spots. As the alloy is more reactive than pure Al, it undergoes easier oxidation which results in increased heat of reaction and sensitization in the decomposition temperature of AP. The burning rates of Al-Mg alloy pellets increase with the increase in alloy content.The combustion products with alloy contain large amount of hydrogen.

2.Platinum metal : Induction period with Pt is reduced and decomposition rate is increased when AP is crushed in platinum crucibles. This activity is due to the ability of platinum to catalyze the oxidation of ammonia.

Non- metals :

Carbon and Sulfur[29] :

Pure AP decomposes in two stages at 330 and 460°C Addition of charcoal causes the exothermic decomposition of AP and oxidation of carbon at about 310-330°C. On the other hand , presence of sulfur does not alter the decomposition of pure AP, but binary mixture of C+S increases the temperature of decomposition and oxidation of carbon and sulfur and a single exotherm occurs at nearly 350°C.

MECHANISM ON CATALYTIC EFFECT

Interaction between AP and Catalyst.:

Admixture of oxides essentially changes the direction and products of decomposition of AP. The mechanism mainly depends on the data of activation energy values.

The same activation energy at low temperature decomposition for pure AP is attributed to electron transfer process. The role of catalyst is to promote the transfer of electron from perchlorate ion to ammonium ion. A complex is formed with metal ion $.ClO_4$ radical and NH_3 radical which stabilizes the electron transfer process and the reformation of perchlorate ion is decreased.

The increase in the activation energy can be interpreted as being due to change in the mechanism of the chatalytic decomposition.It was assumed earlier that primary reaction is rupture of Cl-O bond whose dissociation energy 64.3 K Cals/mole.which is much higher .Both electron transfer (32K Cal/ mole) and ClO ion formation play a part in the decomposition of AP. Metal oxides bring down the ClO bond energy significantly and the resultant is around . 40 K Cal/mole.

Since the activation energy of catalyzed decomposition of AP (40-45K Cals/ mole) agreed well with the activation energy of perchloric acid ,it is assumed that the rate determination step is the perchloric acid decomposition on the surface of the oxide.

In case of oxides which inhibit the decomposition process the mechanism slightly differs.The inhibition process is due to formation of less reactive metal perchlorate which is formed either directly or as a result of reaction with perchloric acid.The resulting NH_3 is not removed from the reacting zone and the process is retardation of combustion. Excess ammonia formation due to combination of metal ion with perchloric acid shifts the equilibrium to the left.

Oxides like Fe_2O_3 ,MnO_2 ,ZnO etc. are positive catalyst. They decrease the induction time to zero and increase reaction rate.and decomposition .With MnO_2 and AP in loose powder form 100% decomposition occurs at about

300° C.The most spectacular effect of SnO_2 is, it lowers the ignition temperature by 150°C

Some oxides are doped on AP.Then the decomposition can be attributed to the change in the rate of reaction between AP and oxide.

Modern kinetic investigations brought a fundamental change in the mechanism of uncatalysed AP decomposition. The mechanism is considered to be due to proton transfer irrespective of temperature.In the presence of catalyst of high electron affinity the mechanism may be due to the electron transfer reaction in the condensed phase at low temperature.

A new interpretation is given for oxide catalyst. Perchloric acid formed migrates to the surface of the oxide and undergoes decomposition. The next step is the oxidation of ammonia by the decomposition products of perchloric acid like O ,ClO ,and ClO_2

Above 300° C and also in the combustion of AP where the AP decomposition is significant ,the heterogeneous decomposition of perchloric acid predominates. Since the electron properties of catalysts are decisive in the oxidation of NH_3, the catalysts which enhance both perchloric acid decomposition and oxidation of ammonia are considered as most effective and positive catalysts.

As far as deflagration[5] is concerned , a qualitative explanation of the role of catalyst is given by

Friedman et. al. Catalysts increase the heat flux back to the surface by catalysing the exothermic reaction. At low concentration increase in the heat loss is dominent and hence the heat flux decreases. This makes deflagration at low pressures difficult and thus raises the low pressure limit. The role of catalyst in deflagration is still not understood.

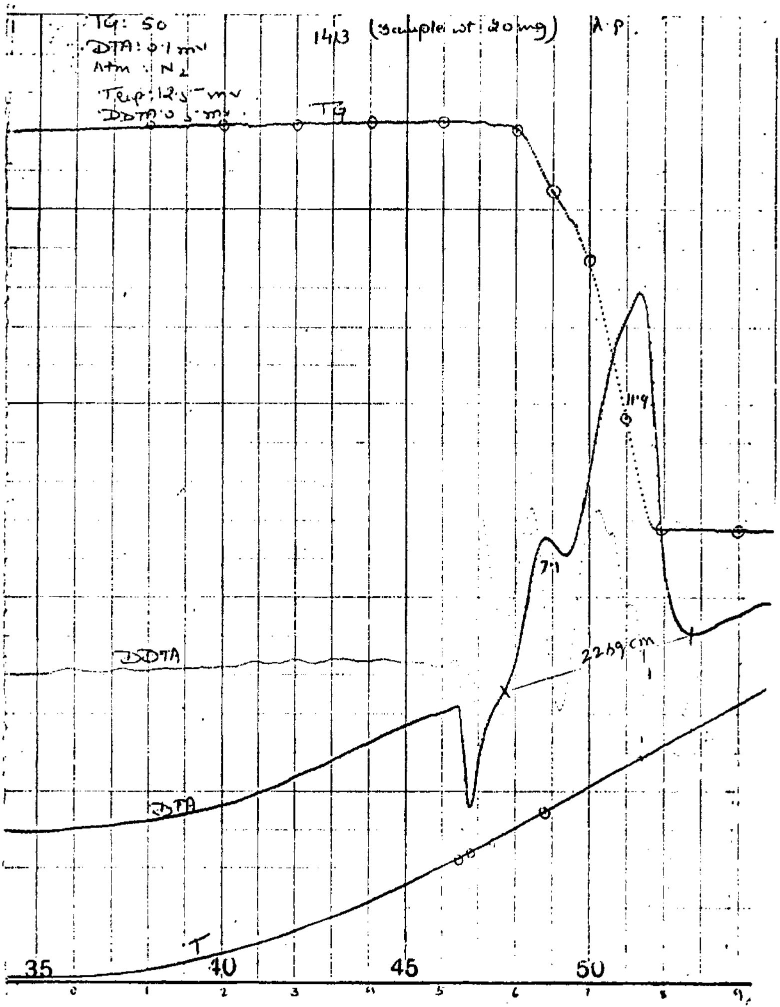
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Fig. 1

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