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6 "A Study of the Decomposition Mechanism of Ammonium Perchlorate"

For the period: 22 Feb. to 1 July 1964

1. Introduction

This project has been undertaken for the purpose of studying the chemical reactions which constitute the decomposition of ammonium perchlorate (hereinafter abbreviated AP) resulting from the application of heat. The order of these reactions and the energies of activation will be sought first, in order that a possible mechanism may be postulated. In addition the effect of catalytic agents will be measured on the activation energies of these reactions. It is felt that, if a better understanding of the rate controlling step in this decomposition can be realized, then a more judicious selection of catalysts are possible to achieve maximum realization of the oxidizing potential of this reaction.

2. Current Efforts

Background information being essential before an attack upon a problem, our efforts during this reporting period have consisted in an exhaustive literature survey on the subject of AP decomposition as well as on topics of related interest, e.g. the decomposition of alkali metal chlorates, perchlorates, nitrates, nitrites and chromates. Some two hundred and thirty references have been checked and studied on these topics.

In order that our results could be utilized by other laboratories, we were instructed that standard, commercially available equipment should be used rather than individually fabricated pieces. Procurement of these commercial items has proved to be a slow process and has caused a serious delay in the start of data collection, however, delivery is now assured in

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the immediate future.

3. Experimental Theory

Differential thermal analysis (DTA) will be employed to obtain the data necessary for the evaluation of reaction orders and activation energies.

DTA is the technique of measuring the heat effects associated with chemical changes that occur when a substance is subjected to a uniform increase in temperature. This heat effect, which occurs during a chemical change, is measured by a differential method. A sample holder, containing two symmetrically located and identical chambers, is placed in a furnace controlled by a programmer which causes the temperature to increase at a constant and prescribed rate. Each chamber contains an identical temperature detection device so connected electrically that the difference in temperature of the chambers is recorded on the Y axis of a recording plotter, which at the same time, records time on the X axis, i.e. sample holder temperature since the rate of heating is constant. The sample being studied is placed in one chamber and a thermally inert substance, or reference, in the other chamber. If the sample becomes cooler or hotter than the reference due to a chemical or physical change, a peak in a downward and upward direction respectively will be produced on the plot.

Since the area under the peaks is proportional to the heat change involved, then knowing the sample weight, a quantitative measure of the heat of the reaction is possible.

This total heat of reaction ΔH can be expressed in the form of an equation (Ref. 1 & 2)

$$\Delta H = (gk/m) \int_a^c \Delta T dt \quad (1)$$

where g = geometrical shape constant for the furnace, k = thermal

conductivity of the sample, M = mass of the reactive sample, ΔT = difference of temperature at center of sample and reference at some particular time, dt = differential of time and a and c represent points on the graphical plot where the thermograph peak starts and stops.

The use of this expression is predicated upon certain assumptions. Terms g and k are constants, since they depend upon the furnace used. Temperature gradients within the sample are neglected and too the area under the curve is considered to be independent of the specific heat.

To use DTA to obtain information concerning the kinetics and reaction order of a simple decomposition reaction such as, solid \rightarrow solid + gas, one may describe such a reaction by the following differential equation (Ref. 3)

$$dx/dt = A(e^{-E/RT})(1-x)^n \quad (2)$$

where dx/dt is the rate of the reaction, x is the fraction reacted, n is the empirical order of the reaction, A is the frequency factor, R is the gas constant and T is temperature in degrees Kelvin. This expression holds true for any value of T , whether constant or variable, so long as x and T are measured at the same instant.

For immediate purposes of simplification let us consider the order n to be unity.

When the reaction rate is a maximum, i.e. at the peak temperature, T_m , of the thermograph, the derivative with respect to time is zero, so solving the above equation (2) for $d/dt(dx/dt)$:

$$d/dt(dx/dt) = dx/dt([E/RT^2][dT/dt]) - A e^{-E/RT} \quad (3)$$

and setting the left hand side equal to zero, we get at temperature, T_m ,

$$A e^{-E/RT_m} = (E/RT_m^2) dT/dt \quad (4)$$

From this equation (4) the following expression is obtained (Ref. 4)

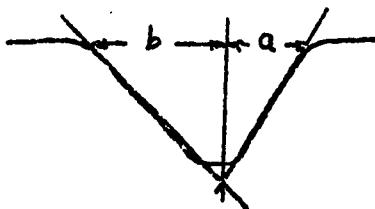
$$d(\ln \phi / T_m^2) / d(1/T_m) = (-) E/R \quad (5)$$

where $\phi = dT/dt$, the heating rate, must be constant in a given experiment.

Although the above equation (5) was derived for a first order reaction it is now known to hold regardless of the reaction order (Ref. 4).

In DTA work T_m for a given value of ϕ is determined by both A and E. If ϕ , which depends only on E is changed, T_m is changed. To find the variation of T_m as ϕ is altered then a plot of $\ln \phi / T_m^2$ vs. $1/T_m$ should give a straight line of slope (-) E/R. With E found then A can also be calculated using equation (4).

The order of the reaction, n, can be found from the shape of the DTA curve peak. As n is decreased the peak becomes more asymmetric. Kissinger (Ref. 4) has developed a "shape index" defined as the absolute value of the ratio of the slopes of the tangents to the curve at the inflection points of $S = a/b$, which is illustrated as follows:



The order of the reaction is given by

$$n = 1.26(S)^{1/2}$$

In our experiments known masses of AP will be heated at various, constant heating rates and the DTA curves measured. From these curves the

values ϕ , T_m , ϵ and b will be obtained so the E , A and n may be calculated. The repeat of these determinations with variation in such things as the atmosphere and pressure on the sample, the presence of catalytic agents and particle size will give us an indication as to how these variables influence the activation energy and/or the order of the AP decomposition.

4. Mechanism of Ammonium Perchlorate Decomposition.

It is expected that when one follows the energy changes by DTA as solid AP is heated from room temperature to approximately 450° C. a complex picture will unfold, for it is evident that at least four different physical and chemical changes may occur.

There is the crystal transformation from orthorhombic to cubic that occurs at 240° C. Below and above 350° C. the mechanism of decomposition is not the same. Such will be hereafter noted by the terms low and high temperature decomposition. Sublimation also is observed to start at a temperature of as low as 130°C. These constitute the four prime changes and in some cases they may occur concurrently.

Quite a number of factors also seem to have a bearing on the rate and nature of the decomposition. These parameters are the nature and pressure of the atmosphere above the AP, particle size of the AP, the presence of impurities and the previous history of the sample of AP.

The experimental work on the AP isothermal decomposition reactions recorded to this time for the most part has involved the recording of pressure-time changes. Such a method, though, cannot be used above 440° C. for the reaction becomes too rapid to be followed manometrically. In this case only induction periods were noted.

The crystal transformation. Bircumshaw and Newman (Ref. 5) concluded that the occurrence of the crystal transformation at 240°C. does complicate

the kinetic results but does not alter the general picture of the electron transfer mechanism. The more stable nature of the cubic form somewhat counterbalances the increased thermal rotation of the ions present. It has been observed (Ref. 6) that the maximum rate of decomposition in vacuo decreases at 240° C. where this crystal change occurs and continues to decrease to 250°C. then starts to rise again. It is possible that the maximum stability of the cubic crystal occurs at the latter temperature, however, it could be that the transition is slow and is not complete until that temperature is attained.

The heat of transition at 240° C. (Ref. 7) has been reported to be 2.3 ± 0.2 kcal/mole. The computed density (Ref. 7) of the cubic form is 1.76 g/cc as compared to 1.95 g/cc for the rhombic form. This means that as the temperature is raised through this transformation there will take place enough of a volume increase to cause strains and distortions to occur in the solid AP. This is contrary to Bircumshaw and Newman (Ref. 5) who report that the lattice distances are reduced when the cubic form is realized.

The sublimation process. It is the opinion of Inami et al (Ref. 8) that the dissociation pressure of AP is an important parameter in the analysis of the combustion mechanism of solid propellants based upon this oxidizer. They measured the dissociation pressure of AP in the temperature range of 247-347° C. by a transpiration method. Their data indicated that AP sublimates by the process of



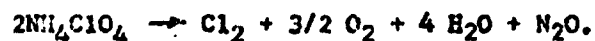
The heat of dissociation was found to be 58 ± 2 kcal/mole in this temperature range. Bircumshaw and Phillips (Ref. 35) report the energy of activation for sublimation to be 21.5 ± 2.78 kcal/mole.

It was observed that both low temperature decomposition and sublimation occur simultaneously, however, no evidence of any effect of the thermal decomposition on the sublimation was seen. Such confirms the report of Bircumshaw and Newman (Ref. 6) that sublimation depends only upon temperature and to a certain extent on pressure.

Some NH_4Cl was found in the sublimate. This must arise from the reaction of Cl_2 formed in the thermal decomposition with the NH_3 . If sublimation is tried in an atmosphere of NH_3 , only NH_4Cl is collected as no AP will sublime, since the NH_3 suppresses the perchloric acid vapor pressure to nearly zero.

Because of this tendency to sublime then it is obvious that the nature of and the type of atmosphere in contact with AP will indeed have a bearing on its decomposition process.

The low temperature thermal decomposition. Below 350°C . (Ref. 6 and 9) the products of the thermal decomposition can be accounted for by the reaction



Bircumshaw and Newman (Ref. 6) demonstrated that this low temperature reaction always ceases after about 30% decomposition, leaving a residue of NH_4ClO_4 which is identical, chemically and physically, with the undecomposed product except in one respect (Ref. 9). The residue had a surface area corresponding to blocks of material of a size of the same order as that of mosaic blocks in crystals. Apparently the low temperature reaction involves only decomposition of strained materials in the inter-mosaic grain boundaries. Visual observations of whole crystals (Ref. 6) at various stages of the reaction show that nuclei are formed on the surface and these grow three-dimensionally until a coherent interface is built up which then penetrates the crystal. An analysis of random

nucleation at potential nucleus forming sites, followed by three dimensional growth, leads to a kinetic equation which contains two constants, one of which depends upon the energy of nucleation and the other on the energy of linear growth. These energies reported by Galwey and Jacobs (Ref. 9) are as follows:

	Energy of formation of nuclei	Energy of Growth
whole crystal -----	31.7 kcal./mole	16.9 kcal./mole
powder-----	31.7 "	22 "
pellet-----	31.7 "	30.1 "

The increase in the activation energy for nucleus growth in the sequence crystal: powder: pellet, is a most striking feature of the reaction.

The nature of the residue indicated that the low temperature reaction is confined to intergranular material. The low temperature reaction will occur only when the gaseous products formed are able to escape and in strained material where the activation energy for the rate determining step is less than in a perfect crystal. This means the reaction starts at the junction of mosaic blocks (nucleus formation) and spreads through intergranular material (growth) until this is all consumed leaving a mass of loosely attached mosaic blocks which are unreactive unless disturbed or exposed to water vapor for certain periods of time.

The increase in energy of growth in the series crystal: powder: pellet may be ascribed to differences in physical nature of the materials. A whole crystal consists of coarse mosaic blocks, separated by comparatively large-angle grain boundaries, whereas a pellet contains a large number of small-angled grain boundaries with less misfit. The powder is intermediate between crystal and pellet.

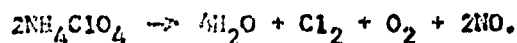
Above the transition point (240° C.) the changes in activation energy are much smaller (25.3, 24.6, 29.9 kcal./mole for crystal, powder and pellets respectively). Apparently the phase change involves a reorganization of the mosaic structure which gives a much finer subgrain net work. Nucleation is followed by propagation of the reaction down this net work in what is essentially one-dimensional growth.

Galvey and Jacobs (Ref. 9) consider the decomposition to involve first the formation of the molecular complex, NH_4ClO_4 , i.e. an electron is transferred from the ClO_4^- ion to the NH_4^+ ion. The reaction must start on the surface where there is an imperfection which will allow this electron and its corresponding positive hole to be trapped long enough for the molecular complex to decompose. From the complex NH_4ClO_4 two molecules of water are removed thereby leaving a nitrogen atom and a molecule of ClO_2 . This is followed by the formation of N_2 , Cl_2 and $[\text{O}]$. N_2 and $[\text{O}]$ then can react to form N_2O .

The high temperature decomposition. (Ref. 5, 6 and 10). To study the decomposition of AP above 350° it is necessary to introduce an inert gas under pressure over the sample, in order to minimize sublimation. Between 350-450° C. the AP decomposition obeys the power law

$$p = kt^n$$

where p = pressure evolved in a constant volume system in time t , and k and n are constants. n though was noted to vary somewhat irregularly with temperature between the values of 0.5 and 1.0. The reaction was deceleratory throughout and, in contrast to the low-temperature decomposition, resulted in complete decomposition of the salt. It is noted that the products also differ from the low temperature reaction in that NO instead of N_2O was produced. The following equation is representative:



Because the two different reactions are occurring in the temperature range 300-330° C. results are difficult to reproduce.

Decomposition in this high temperature zone probably takes place by (1) the transfer of a proton from the ammonium ion to the perchlorate ion, thereby forming free ammonia and perchloric acid, then (2) the perchloric acid decomposes quickly to form water and Cl_2O_7 . (3) Next the Cl_2O_7 yields Cl_2 and oxygen, which, (4) oxidizes the ammonia to NO and water.

The energy of activation for this reaction has been evaluated at 40 kcal./mole.

J. Powling and Smith (Ref. 11) studying the surface temperature of burning AP have concluded that the surface temperature of the AP is only of incidental importance at moderate pressures and that the gas phase reaction between the ammonia and perchloric acid control the rate of consumption of the oxidizer.

The thermal explosion of ammonium perchlorate. Above 300° C. the reaction is too fast to be followed by the same experimental techniques used for the other temperature ranges. Here only the induction period could be measured (Ref. 12). After this induction period there is a sudden large pressure change which is often accompanied by a flash of light.

Results indicate that the low temperature process, despite its lower activation energy, still occurs more rapidly than the higher temperature process in this case, being 99% complete in less time than required for the explosion, so that it cannot account for the explosion. Explosion times show that the explosion occurs when the residue from the intergranular (low-temperature) reaction is about 1/3 decomposed. The activation energy measured to be about 42.5 kcal./mole and as such supports this conclusion.

The influence of catalysts on the ammonium perchlorate decomposition.

Many materials have been tried as positive catalysts to speed up the rate of thermal decomposition of AP. The following is a partial list of compounds, which have been used with perchlorate salts.*

<u>Substance used</u>	<u>Reference</u>
MgO-----	(26)
CuO-----	(13) & (14)
Cu ₂ O-----	(15)
Cu salts-----	(16)
CrO ₃ -----	(13) & (17)
CrO ₂ Cl ₂ -----	(17)
ZnO-----	(18) & (19)
CdO-----	(33)
NiO-----	(34)
Ni ₂ O ₃ -----	(17)
Fe ₂ O ₃ -----	(20) & (21) & (6)
MgO-----	(17)
Co ₂ O ₃ -----	(17)
Co ₃ O ₄ -----	(17)
MnO ₂ & other Mn oxides-----	(17) & (16) & (23) & (27) & (28) & (6)
KMnO ₄ -----	(16) & (22)
Rhenium compounds-----	(22)
Carbon-----	(24)
Al ₂ O ₃ -----	(23) & (6)
CaO-----	(6)

* Note-References 29, 30, 31 and 32 deal with catalysts used with KClO₃ decomposition. Some 75 catalyst systems are listed in these four references.

The most extensive effort seems to have been directed toward the use of MnO_2 , and the work of Galwey and Jacobs (Ref. 23) seems to represent one of the most complete and authoritative studies on this phase of the problem.

Using mixtures of 10% MnO_2 and 90% AP their time-pressure measurements clearly pointed up the fact that in the temperature range of 200-220° C, the reaction occurs in two distinct stages. There is an initial fast reaction which is followed by a much slower reaction that is deceleratory throughout. Both by analysis of the graphical plots and the collection of the products it was evident that the second reaction is independent of the MnO_2 .

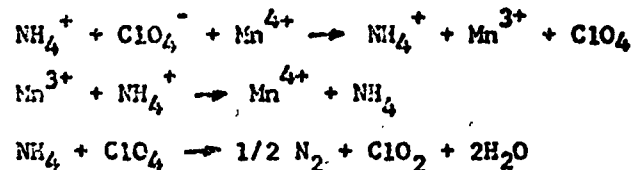
All observations tended to indicate that the catalytic activity is the result of physical contact between the MnO_2 and the AP. The degree of compression of the sample always produced an effect on the kinetic results. The first reaction stops then when the particles no longer present a salt/oxide interface.

Those compounds which have been observed to give any positive catalytic effect contain metals that can demonstrate variable valence or oxidation states. Not only different oxidation states, but these states must be of about equal tendency to form. This was most clearly demonstrated in the work (Ref. 22) of Brown and Woods comparing manganese and rhenium compounds as catalytic agents in the AP decomposition. Whereas manganese compounds were always found in mixed valence states at the conclusion of a reaction regardless of the starting valence condition, the rhenium always ended up in the very stable perrhenate state. Low valence rhenium compounds showed initial catalytic activity but this ceased as soon as the stable perrhenate condition prevailed. Manganese on the other hand showed continuing catalytic activity.

Galwey and Jacobs (Ref. 23) found little change in the activation

energy of AP decomposition on adding the catalyst. This is apparently due to the fact that the catalyst has nothing to do with the initial and largest energy consuming step which is the transfer of the electron from the perchlorate ion to the ammonium ion and the formation of a positive hole. The role of the catalyst is to increase the life of the molecular complex thereby diminishing its tendency to revert to the ions. The presence of the Mn(IV) must do this by helping to delocalize the molecular electron orbital.

The mechanism proposed can be represented as:



In the uncatalyzed reaction much more O_2 is noted to be set free as compared to the catalyzed one. Such O_2 must originate from the decomposition of the ClO_2 . In the catalyzed reaction the reaction temperature being lower might account for less decomposition of the ClO_2 .

Jacobs *et al* (Ref. 15) in studying the effect of Cu_2O on the AP decomposition still noted the same activation energy value, and proposed a similar mechanism as noted before but in this case felt that the Cu_2O taking on oxygen might account for part of the effect.

One of the most interesting cases of a metal oxide that is quite effective in promoting the thermal decomposition of AP and which involves a non-variable valence metal is ZnO (Ref. 18). In some cases the reaction was so fast that explosion resulted. From the fact that small amounts of Al_2O_3 increased the effectiveness of the ZnO , while Li_2O decreased its effect, the authors concluded that the role played by the ZnO is one of an electron connector.

One case of a negative catalyst for a similar reaction has been reported (Ref. 25). Lithium perchlorate decomposition is slowed down by adding silver nitrate in 5-15% amounts. The authors advanced the idea that the retardation was due to the silver ions removing chloride ions as insoluble silver chloride. This idea was based upon the rate decrease being a function of the silver ion concentration and also that the effect tended to disappear when the temperature reached the melting point of the silver chloride.

Decomposition of other metal perchlorates. Many studies have been reported on the thermal decomposition of other metal perchlorates and chlorates, both with and without catalytic agents present. In these cases the stability of the cation and the resulting stability of the metal halide lattice means that a different mechanism most likely will prevail. Nothing was found that seemed to have a particular bearing on this immediate problem of AP decomposition. The fact that the cation of AP is subject to oxidation by the anion or products of the anion decomposition makes this a rather unique case.

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