

STRUCTURE AND THERMAL STABILITY OF AMMONIUM PERCHLORATE

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The structure of ammonium perchlorate, the methods used to study its thermal decomposition and the kinetics and the mechanism of the decomposition are critically reviewed on the basis of literature data.

Introduction

Ammonium perchlorate (AP) can be regarded as the most important compound of the perchlorate salts. During the last 10—15 years several hundred publications have appeared on its physical-chemical properties. Very great efforts have also been made in our laboratory to understand its thermal behaviour. One of the reasons for this great interest is the fact that AP has found widespread application as an oxidant in solid rocket propellants. In addition to its technological importance, the properties of the compound have provided the possibility of numerous theoretical studies which have considerably increased our knowledge concerning the thermal decomposition of solid materials. Further, the stability of AP is very sensitive to the presence of various additives, and this permits the investigation of catalytic processes in the solid phase. In the recent years a great progress has been made in understanding the mechanism of the thermal decomposition of AP, so it seems important for further work to summarize the main results and conclusions of the investigations.

In the present publication, the different physical and chemical properties of pure AP are summarized, while the influence of additives on its thermal decomposition will be discussed in a following paper.

Structure and physical properties of AP

AP is a white crystalline substance. Two crystal modifications are known; the reversible crystallographic transition occurs at 240 °C [1]. Values of 2.3 and 2.7 kcal/mole are given in the literature for the heat of transition from orthorhombic to cubic form [2, 3]. In the elementary cell of the low-temperature orthorhombic modification there are four molecules; the dimensions are $a=9.202$, $b=5.816$ and $c=7.449$ Å [4—10]. Four oxygen atoms are disposed tetrahedrally around each chlorine atom, at distances of 1.43 Å. Twelve oxygen atoms are found each ammonium ion, eight at 2.94—3.08 Å; and four at 3.25—3.25 Å [10].

The high-temperature cubic modification has a sodium chloride-like structure. In the elementary cell there are four molecules; $a=7.63 \text{ \AA}$ [11, 12]. A number of studies have been centred on the question of the free rotations of the ammonium and perchlorate ions, which is of particular importance in a description of the decomposition of AP. Recent studies on crystal structure [13], NMR [14, 15], neutron diffraction [10, 16], neutron scattering [17–20], infrared [21] and ESR [22] spectra have clearly shown that both the NH_4^+ and ClO_4^- ions can rotate freely: the NH_4^+ ion in both structures, while the ClO_4^- only in the cubic modification.

The total lattice energy of AP is 143.8 kcal/mole, and the electrostatic energy 149.4 kcal/mole. The value of the Madelung constant is 3.3134 [23, 24].

The densities of the rhombohedral and the cubic modifications are 1.95 and 1.76 g. cm^3 , respectively. The specific heat of AP in the range 15–240 °C is 0.309 cal $\cdot \text{g}^{-1} \cdot \text{degree}^{-1}$, and above 240 °C 0.365 cal $\cdot \text{g}^{-1} \cdot \text{degree}^{-1}$ [25].

In the range 50–240 °C the thermal diffusion of polycrystalline AP varies linearly with temperature, and can be characterized by the following formula:

$$K = 3.59 \cdot 10^{-3} - (4.40 \cdot 10^{-6})T \text{ cm}^2 \text{ sec}^{-1}.$$

The diffusion decreases with porosity. The thermal conduction of AP does not change linearly with the temperature [26].

Detailed studies have been made on the electric conductivity of AP; this is considerably higher than those of the alkali metal perchlorates and halides. The conduction is predominantly ionic, and is very sensitive to the gaseous surroundings. In the range 25–125 °C the conductivity of a sample was decreased by both argon and oxygen. In vacuum, in oxygen, and in argon, activation energies of 25.3, 26.7 and 32.3 kcal/mole, respectively, were obtained [27].

At 227–327 °C. in nitrogen atmosphere, WISE [28] found a value of 32 kcal/mole.

The conductivity of AP decreased proportionally to the increase of the partial pressure of gaseous ammonia. In NH_3 of 0.6 molar ratio, the value of the activation energy was 20 kcal/mole. WISE interpreted the high conductivity of AP by charge transfer, which includes the proton movement. Proton transfer takes place from the ammonium ions at the lattice sites to ammonia molecules at lattice vacancies or in interstitial positions. The neutral ammonia formed may serve as a centre for the transfer of a proton from the neighbouring cation. The transfer of protons is facilitated to a large extent by Schottky and Frenkel defects. The conductivities of AP single crystals and powder mixtures compressed into tablets were practically identical.

Detailed investigations were recently made by MAYCOCK and PAI VERNEKE [29, 30]. Their experimental results can be seen in Fig. 1.

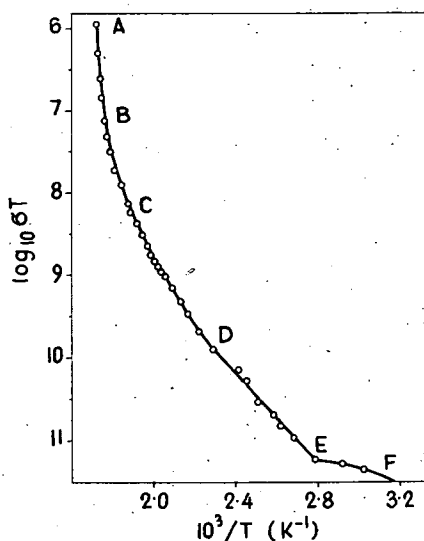


Fig. 1. Electric conductivity of an AP single crystal as a function of $1/T$.

In the plot four stages can be distinguished as a function of the temperature. The break-points are found at 92, 171, 255 and 280 °C. The activation energy of the conductivity is the least in the low-temperature stage between 25 and 95 °C, and this is ascribed to surface conduction. In the stage DE, extrinsic conduction of orthorhombic AP occurs, and in the stage CD intrinsic conduction. The enthalpy of migration of the defects was calculated, and also the enthalpy of formation of a defect-pair; the values obtained were 0.5 and 0.6 eV, respectively. From the low value of the latter it was concluded that the defect structure of AP corresponds to the Frenkel type. With increasing temperature, the activation energy also increases. The break-point at about 255 °C is clearly the result of the phase transition of the AP. It is assumed that intrinsic conduction also occurs in the range BC. In this case a substantially larger value than the previous one, 2.0 eV, was obtained for the enthalpy of formation of a defect-pair; from this it was concluded that a Schottky defect structure is involved. In the range AB a "band-to-band" electron transfer is assumed, and on the basis of the equation

$$\sigma = A \cdot e^{-E/2kT}$$

a value of 5.6 eV was obtained for the activation energy. (It should be mentioned that a value of 6.06 eV was calculated from optical data.)

It was an interesting observation that the electric conductivity of both types of AP first decreases with time, and increases again after a constant stage. The rate of decomposition also varies with time in a similar way. Furthermore, as the rate of thermal decomposition increases after the initial decrease, the conductivity also increases. From the temperature-dependence of the initial conductivity decrease, activation energies of 30 and 20 kcal/mole were obtained for the orthorhombic and cubic modifications, respectively. Since earlier practically identical values were found for the decomposition of AP, it was concluded that the defects play a considerable part in the decomposition of AP, and that the initial decrease of the rate of decomposition is a result of the consumption of the crystal defects.

Characteristics of the decomposition of AP

As mentioned, AP decomposes with a measurable rate over a wide temperature range, between 200 and 530 °C. Of course, the behaviour of the substance changes with increasing temperature. On the basis of the characteristic features of decomposition, the following stages can be distinguished:

1. 200—240 °C;
2. 240—300 °C;
3. 340—430 °C;
4. 440—530 °C.

Between 200 and 300 °C the so-called "low temperature" decomposition, from 300 to 430 °C the "high temperature" decomposition of AP takes place, while above 440 °C, after an induction period depending on the temperature, the AP explodes. Over the entire temperature range sublimation of the AP also occurs.

The most pronounced difference between the low and high-temperature stages is that below 300 °C only about 30% of the AP decomposes, the residual material being pure AP of porous structure with density of about 70% of the original, and increased surface area. The question of the cessation of the reaction will be dealt with later in more detail. Above 340 °C the decomposition of AP is complete, a

solid residue is not formed. The transition between these two stages is not sharp; the range of transition is between 300 and 340 °C. The division of the low-temperature stage into two parts is caused by the crystallographic transition at 240 °C. The kinetic parameters of the decomposition at the transition temperature exhibit a larger change than would follow merely from the change in temperature.

According to BIRCUMSHAW's early observation in the low-temperature region, the formation of nuclei begins on the surface of the crystals or on isolated centres. This is followed by the three-dimensional growth of the nuclei, finally giving continuous interface, which proceeds from the surface to the interior of the crystal. The decomposition comes to an end when this interface reaches the interior of the crystal [80].

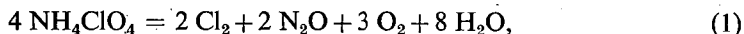
A more detailed study of the characteristics of the formation and growth of the nuclei in a microcinematographic apparatus was carried out by RAEVSKII and MANELIS [81]. It was observed that the nucleation began 20–30 μ beneath the surface of the crystal, the centres of decomposition being composed of spherical nuclei of 1–2 μ m diameter. The centres of decomposition form in an aggregation of nuclei in immediate vicinity. At 230 °C the nuclei move with a velocity of 7–10 μ m/minute.

Viewed from the direction of the rhombic face of the crystal, the decomposition centres are of ellipsoidal form, in form, while from the rectangular face they are hemispherical. The rate of the decomposition increases with increase of the ratio of the areas of rhombic to rectangular faces.

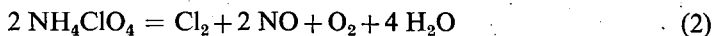
Chemical analysis of the decomposition products

In spite of the numerous investigations, the stoichiometry of the decomposition of AP has not been completely elucidated. Considering the extremely complex nature of the decomposition, the large number of products, and the possibilities of secondary reactions, it is not to be expected that investigations by different research workers should lead to completely similar results. Apart from the analytical difficulties, even small differences in the conditions of the decomposition can lead to changes in distribution of the products.

A detailed chemical analysis of the decomposition products of AP was first carried out by DODÉ [35–37]. He found that the nature and ratio of the decomposition products depend on the temperature. For the reaction taking place below 300 °C, equation



while for the decomposition above 380 °C



was given.

In addition to the above, below 300 °C chlorine dioxide, hydrogen chloride, nitrogen and nitrogen oxides were also detected as minor constituents; similarly, above 380 °C, hydrogen chloride, nitrosyl chloride and nitrogen dioxide were also found.

Beside the above products, BIRCUMSHAW and NEWMAN [38] detected perchloric acid, too. The analytical investigations by ROSSER, INAMI and WISE [99] led to essen-

tially similar results, with the exception that they did not find ClO_2 , whereas HNO_3 and NO_2Cl were detected. It was observed, however, that the Cl_2/HCl ratio decreases with the increase of temperature [39—41]. Similarly, the amounts of ClO_2 and HClO_4 decrease at higher temperatures (above 250—300 °C).

The results of other analytical works agree qualitatively with the above, although there are considerable differences in the quantities and ratios of the products [42—45].

As regards the analysis of reaction products by chemical methods, it must be borne in mind that the vast majority of these refer to the final state of the decomposition, and actually disclose very little about the changes in the products and their ratios in the course of decomposition.

Application of mass-spectrometry and absorption spectroscopy

A deeper insight into the processes of the decomposition has been afforded by mass-spectrometric studies. From the point of view of the clarification of the mechanism of decomposition, studies aiming at the establishment of the primary process of the decomposition can be considered as particularly valuable. Difficulties arose from the fact that sublimation occurs parallel with the decomposition and the products of sublimation may also decompose. HEATH and MAJER [46] heated the AP in a furnace adjacent to the ion-source. The lowest temperature range at which decomposition was detected, was 111—120 °C. Formation of HClO_4 , NH_3 , HCl , Cl_2 , O_2 and oxides of nitrogen was observed.

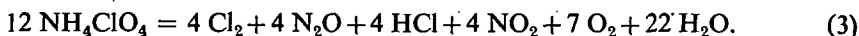
There was no indication of NH_4ClO_4 molecular complex. They considered their results as a proof of the decomposition of AP taking place by proton-transfer. However, in the experimental method used, the products formed during the heating of the sample reach the ionizing radiation after a rather long time (1—100 msec), and this excludes the identification of the initial products.

Using a similar method, GOSHGARIAN and WALTON [47] established the formation of O_2 , H_2O , Cl_2 , N_2O , NO and NO_2 , but they did not find perchloric acid. Their measurements were made at 140—250 °C with AP pre-treated at 200 °C for two days.

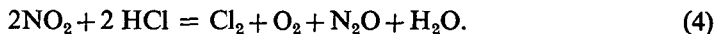
MAYCOCK *et al.* [48, 49] carried out measurements in a system of constant volume, connected to a time-of-flight mass-spectrometer. The disturbing effects of sublimation were eliminated in their measurements, but the possibility of the secondary reactions could not be entirely excluded. The main products of decomposition at 230 °C were: O_2 , Cl_2 , N_2O , in the ratio of 3:2:2 and H_2O ; HCl and N_2 were also found. These results supported the reaction (1) above. The N_2 and HCl found was ascribed to the secondary gas-phase reactions. Experiments carried out in a Knudsen cell indicate that up to 160 °C no detectable species were produced due to the decomposition. The decomposition products identified by HEATH and MAJER at lower temperatures are very likely products of decomposition of the sublimate due to the electron bombardement.

Using a quadrupole mass-spectrometer, HERLEY and LEVY [50] analyzed the products of decomposition at 227 and 235 °C up to about 80% conversion. Their results differed from the results of MAYCOCK only in so far as they could not detect Cl_2^+ .

On the basis of the products found in vacuum with a Bendix time-of-flight mass-spectrometer, PELLET and SAUNDERS [51] proposed the following reaction:



Comparison of this equation with that put forward by DODÉ leads to the equation



This experimental method provided the possibility of establishing the primary decomposition products, since, owing to the low pressure, the probability of secondary reactions is very slight. On the other hand, sublimation cannot be excluded.

It was found that the formation of HClO_4 increases with increasing temperature, but is independent of the extent of decomposition. The ratios $\text{N}_2\text{O}/\text{Cl}_2$, HCl/Cl_2 and NO_2/Cl_2 were close to unity.

In more detailed studies, which were extended to higher temperatures, the decomposition products of AP irradiated by a ruby laser were examined in vacuum. This method ensured the rapid heating-up of the sample [52]. Formation of ammonia and perchloric acid was detected immediately, at the instant of irradiation. However, the perchloric acid rapidly decomposed to ClO_2 and HCl . It is surprising that only a rather slight decomposition of the ClO_2 was observed, and under the given experimental conditions it proved to be substantially more stable than perchloric acid. It was shown that

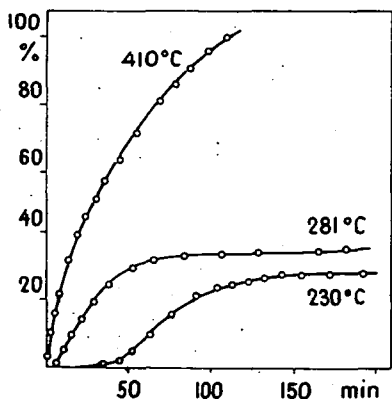


Fig. 2. Percentage decomposition of AP at different temperatures.

with the decrease of the temperature from 240 °C, the ratios of H_2O , O_2 , Cl_2 , N_2O and NO_2 to HCl all decrease.

BOLDYREV *et al.* [53—56] placed the AP crystals in a thin layer on a Ti ribbon which was heated up rapidly to the desired temperature in a mass-spectrometer. The spectrum of the products of decomposition of AP in the range 250—500 °C was practically identical with the sum of the lines appearing in the mass-spectra of ammonia and perchloric acid.

At 400 °C, 10^{-3} sec after the beginning of the reaction, the relative intensities of the lines due to the products were as follows:

m/e	ion	intensity %
16	NH_2^+	53
17	OH^+ , NH_3^+	93
35	Cl^+	13
51	ClO^+	13
67	ClO_2^+	63
83	ClO_3^+	100
100	HClO_4^+	54

A mass-spectrometric study of the secondary reactions following the dissociation of AP was made at 400 °C [56]. The major products of the reaction were Cl_2 , O_2 , N_2O and H_2O . N_2 , NO and HCl were also detected in small quantities. The $\text{Cl}_2/\text{HClO}_4$ ratio underwent a characteristic change during the decomposition. If the ratio was initially less than 1, it increased during the decomposition and finally became greater than 1.

MAYER and SMITH [57] investigated the products of the gas-phase decomposition of AP. In their experiments, AP previously treated at 300 °C was evaporated at 320 °C and the AP in gas state was led in a stream of N_2 into a reaction zone heated up to various temperatures. The reaction space was connected to a mass-spectrometer by means of a "pinhole".

Among the products of the condensed-phase decomposition at low temperature, NH_3 could already be detected at 270 °C, but it was found in well-measurable amounts only at about 300 °C. Perchloric acid could not be detected, although the sublimation of AP was observed. The products of gas-phase reaction were H_2O , O_2 , HCl , H_2 , N_2O , NO_3 , Cl_2 , ClO_2 , HClO and NH_2Cl .

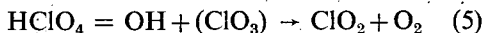
The last two products had not been observed previously.

The products of the gas-phase reaction were established by subtracting the amounts measured at 300 °C from those found at 468 °C.

The gas products were practically identical with those found at low temperature. A significant difference was that the amount of NH_3 was smaller. The composition of the products indicates that in the gas-phase reaction the NH_3 is oxidized to N_2O , NO_2 and N_2 .

Valuable results in understanding the decomposition of AP were obtained by the joint use of flash photolysis and kinetic spectroscopy [58]. A great advantage of the method is that the system can be analyzed already 2 μsec after the irradiation. Fig. 3 shows the relative concentrations of the radicals produced by the flash as a function of time.

The two main products found 20 μsec after the flash are ClO_2 and OH . With time the line due to ClO_2 becomes weaker and after 100 μsec it is hardly detectable. It is an interesting result that the intensity of the NH radical formed in the oxidation of the NH_3 scarcely depends on the concentrations of other radicals or on time. The concentration of NO increases with time, which points to its end-product character. The results obtained prove the dissociative decomposition of the AP and the following reaction of the perchloric acid:



The changes in concentrations of the radicals are explained by the decomposition or oxidation of ClO_2 and NH_3 ; this was confirmed in a separate experiment with ClO_2 .

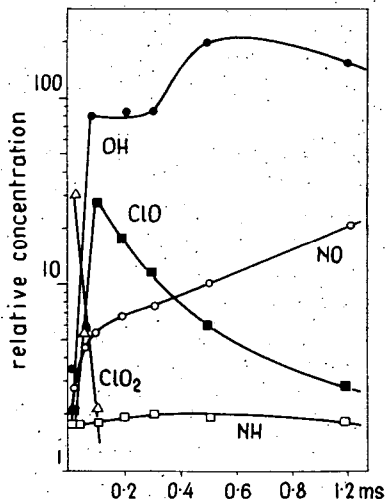


Fig. 3. Relative concentration of radicals formed in the decomposition of AP as a function of time.

Further details concerning the chemistry of decomposition of AP were revealed by studies with a CO₂ laser [59]. The sample was pyrolyzed by a rapid heating of 222 cal · cm⁻² · sec⁻¹. The analysis of the decomposition products was carried out after consecutive heat-impulses, in the region of quasi-constant-rate decomposition and on cooling of the sample. The high vacuum of 10⁻⁶ torr permitted the direct analysis of the products of pyrolysis and the establishment of their formation rates. By plotting the intensities of the ion-current of 27 eV as a function of time, 3 stages can be distinguished.

Period I is characterized by the heating and the increase of the formation of the products; in period II the quasi-constant-rate condensed-phase decomposition takes place; and period III, after switching off the laser irradiation, the deceleratory stage of decomposition follows.

In period I, NH₃ and HClO₄ are always the initial products. Even after 5 msec they have been formed in significant amounts. At a heating rate of 70 cal · cm⁻² · sec⁻¹ the maximum rate of formation of HClO₄ is attained within 25 msec. The NH₃/HClO₄ ratios decreased with time from the initial relatively high value, and this was explained by the initially easier desorption of the NH₃, and by its relatively larger participation in the condensed-phase reaction in the later part of the period. A delay of about 2—5 msec was found between the rates of formation of NH₃ and of HClO₄, which is not surprising if it is assumed that the adsorption of the two substances on the surface is of different strength.

On the decrease of the NH₃/HClO₄ ratios found after a well-measurable induction period — the products of the solid-phase decomposition: H₂O, O₂, Cl₂, HCl, N₂O and N₂ appeared. After 100—200 msec their rates of formation had already become constant. From the middle of period I to the end of period II, only a small effect on the ratio of the products is exerted by the reaction time and the heating rate with the CO₂ laser. In addition to the above main products, it was also possible to confirm the presence of the ClO₃ radical during period II.

While ClO₂ was one of the main decomposition products in the pyrolysis of AP containing oxides, in the present case it did not form in significant amounts neither in the first nor in the second period.

In the third period (when the laser irradiation had ceased), the rate of formation of NH₃ and HClO₄ decreases, but simultaneously the rate of formation of the decomposition products (Cl₂ and N₂O) temporarily increases, indicating that with the decrease of the desorption of the NH₃ and HClO₄ the condensed-phase decomposition comes into prominence. With further decrease of the temperature the rate of this process decreases, too.

The results confirm the importance of the proton-transfer process, and point to the fact that, in the second period, the NH₃ and HClO₄ adsorbed on the solid AP can partly react with each other, and can also partly be desorbed. There is a dynamic equilibrium between the two processes. The fact that, in spite of the high vacuum and the elevated temperature, the condensed-phase decomposition is considerable shows that at high pressure, in the ignition of AP-containing propellants, this reaction plays a substantially greater part than was presumed earlier.

A mass-spectrophotometer was used to study the products forming on the pyrolysis of AP and of organic polymers, but these studies provided very few data concerning the course of the decomposition of pure AP [60, 61].

Differential thermal analysis (DTA) studies

Because of its simplicity and rapidity, the DTA method is frequently applied for determining the thermal stability of AP, and especially the role of additives [62—78].

On the DTA curve of AP an endothermic peak at about 240 °C can be found, while above 300 °C two exothermic peaks attributed to its decomposition can be seen. The endothermic change is the result of the transition from the orthorhombic to the cubic modification of AP. The first exothermic peak appears directly after the phase change at 280—300 °C, and the second at about 440 °C. Accordingly, the low and high temperature decompositions are revealed on the DTA curve of the substance. In the works of various authors only slight differences are to be found regarding the temperature of the crystal transition. Much greater differences are, however, found in the occurrence of the two exothermic peaks characterizing the decomposition of AP. These are partly due to the factors generally affecting the DTA curves: particle size, heating rate, amount of sample, etc. Because of the high sensitivity of the stability of AP to the presence of foreign substances, it is, however, the grade of purity of the material which plays the greatest role in the deviations.

The temperatures at which the peaks appear vary also sensitively with the gas atmosphere. In the experiments of STONE [62], in vacuum, the decomposition of the substance is accompanied by only one exothermic heat change at 300 °C. In nitrogen, exothermic heat changes appear at 280 and 400 °C, while ammonia completely suppresses the decomposition occurring at the lower temperature, and an exothermic heat change appears only at 400 °C. The first exothermic heat change can be made to disappear, or to decrease in extent, by repeated heat-treatment (heating, interruption, cooling, repeated heating).

In Fig. 4 a characteristic DTA curve of AP taken in air is presented.

A number of experiments have been made with DTA measurements to determine the activation energies of the decomposition. The value of the activation energy (32.0 kcal/mole) determined by DANIELS [63] shows the best agreement with the values obtained under isothermal conditions. In other cases the differences are very great.

Taking into account that the AP dissociates into ammonia and perchloric acid at higher temperatures, which is an endothermic process, it would have to be expected that (in so far as the reaction between the products of the dissociation is slow or can be eliminated in some way) an endothermic heat change characteristic of the dissociation process would also appear on the DTA curve for AP. In earlier studies, only STONE [62] found an endothermic heat change above the transition point at 400 °C, when the DTA curve of the AP was taken in vacuum. ALEXANDROV and GLADKIKH [64] developed a more sensitive method for detecting heat changes in AP. Mixtures of AP and an inert diluting material were placed between titanium ribbons and heated electrically to the desired temperature in 1×10^{-2} sec in vacuum. The heat change produced in the material was followed by measuring the tempera-

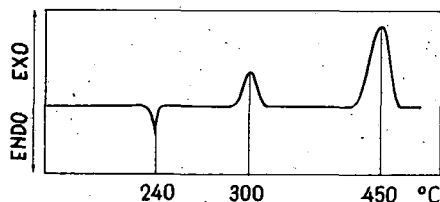


Fig. 4. Differential thermal analysis (DTA) curve of AP.

tures of the lamellae. They observed an endothermic heat change already at 300 °C which was claimed to belong to the endothermic dissociation of AP. It is, however questionable whether the endothermic heat change connected with the phase transition had not distorted the experimental result.

Kinetic investigations

The kinetics of the decomposition of AP have been studied most generally by the measurement of the pressure of permanent gases as a function of time. A requirement of the experimental method is that the O₂/N₂ ratio should be identical during the progress of the decomposition and, in addition, that the ratio of the permanent gases to the other gases should not change either. According to the analytical results of BIRCUMSHAW and NEWMAN [38], in the range 240—320 °C these conditions are approximately fulfilled. At higher temperatures, in order to avoid sublimation, the use of inert gases is necessary. The decomposition has been also followed by measuring the total pressure or the volume of the gases formed or the loss in weight of the substance.

An important observation concerning the applicability of these methods was that, under identical conditions and using the same materials, the measurement of the weight loss and the permanent and total gas pressures resulted in practically identical α vs. t curves up to $\alpha=0.7$ [79].

Recently the decomposition of AP has been followed by numerous other methods. Measurements of kinetic nature have been carried out under isothermic and adiabatic conditions.

Considering that the decompositions of AP are fundamentally different in the low (200—300 °C) and high (330—440 °C) temperature regions, it appears reasonable to discuss the kinetic studies accordingly.

The low-temperature reaction

Between 200 and 300 °C the decomposition of AP is of an autocatalytic nature (Fig. 1). According to an early microscopic investigation, in the time-lag and acceleration stages of the decomposition, the formation and growth of the nuclei take place, while in the decay period the reactions zones coalesce [80].

Numerous kinetic equations have been used for the mathematical approximation of the decomposition curves obtained under isothermic conditions. The use of any kinetic equation is empirical until direct observation of decomposition centres confirms the model based on it.

For the kinetic analysis of the acceleration period the exponential law

$$p=(kt)^6 \quad (7)$$

was applied, while the equation

$$-\log(p_f-p) = kt + C \quad (8)$$

was used for analyzing the deceleratory period, where p_f = the final pressure measured at the cessation of the decomposition, while p is the pressure measured at time t .

The decay period was also evaluated with the "contracting cube" formula

$$1 - (1 - \alpha)^{1/3} = kt \quad (9)$$

where α = the degree of decomposition at time t .

Satisfactory results were obtained for the acceleration and decay stages of the decomposition by using the Prout—Tompkins relations

$$\log \frac{p}{p_f - p} = kt + C \quad (10)$$

The best fit was obtained in most cases with the Avrami—Erofeyev relation

$$[-\log(1 - \alpha)]^{1/n} = kt + C \quad (11)$$

with $n=3$ or 2.

Recent optical and electron microscopic study of the formation and the three-dimensional growth of nuclei seemed to justify the use of the Avrami—Erofeyev equation (11). The preferred direction of growth with branching along (150) planes comprises some features of the Prout—Tompkins model. However, some inadequacy in their application was also disclosed in both cases.

From the numerous kinetic investigations, we first mention those which also included the study of some factors, or were related to the formation of some special products, or kinetic measurements based on the direct observation of decomposition centres.

Fairly large deviations are found in the kinetic data, especially in the values of the activation energy. This may be due to different kinetic interpretations of the decomposition curves and partly to the fact that the activation energy values measured by the individual authors refer to different stages of decomposition. However, the decomposition of AP and its activation energy can be affected by the prehistory and pretreatment of the AP, by the dimensions of the crystal, by the size of the sample, etc. The important role of the above factors was shown by the work of GALWEY and JACOBS [84], who studied the decompositions of single crystals, powder and tablets under identical conditions, and found increasing activation energy values in the above order.

OSADO and SAKAMOTO [40] found that the increase in grain dimensions from 25 μ to 56 μ resulted in a slight decrease of the activation energy for the decomposition of the cubic modification, from 23.3 to 21.5 kcal/mole [40]. Further increase of the grain size (to 80 μ) had no effect.

Experiments carried out with the adiabatic method showed that the increase of the grain size from 43 μ to 88—123 μ causes an increase of 3.6 kcal/mole in the value of the activation energy [85]. The rate constants in this case were determined by the equations

$$\frac{dT}{dt} = k_a(T - T_i) [1 - (T - T_i)/\Delta T^x] \quad (12)$$

$$\frac{dT}{dt} = nk_n(\Delta T^x)^{1/n}(T - T_i)^{(m-1)m} [1 - (T - T_i)/\Delta T^x] \quad (13)$$

where T_i is the initial temperature, and ΔT^x is the increase in temperature during

the complete reaction ($\alpha=1$). Equations (12) and (13) can be considered as modified forms of the Avrami—Erofeyev and Prout—Tompkins equations.

The value of ΔT^* was calculated with satisfactory accuracy by assuming the following equation for the decomposition



It should be noted that the activation energy values are significantly smaller than in the case of measurements under isothermal conditions. A possible reason of this is that the disturbing effect of self-heating may be eliminated under adiabatic condition.

RUBTSOV and MANELIS [81] found that the rate of growth of the decomposition centres is ten times greater in the longitudinal direction than in the transverse direction. The activation energies of the growth are 31 ± 1 and 33 ± 1 kcal/mole, respectively, in these two directions. The activation energy of the growth of the nuclei of the cubic modification is 17 kcal/mole. The formation of the decomposition centres is controlled by the growth of the single nuclei. These are spherical in shape and extend over the entire crystal.

The microscopic measurements of KRAEUTLE [83] made it very probable that the activation energies of the decomposition of AP can even be affected by the shape of the AP crystals.

The kinetics of the decomposition of rhombic AP was studied by measuring the progress of the interfacial reaction with an optical microscope. The temperature range was 221—231 °C. The formation and growth of the nuclei and the interface decomposition could readily be distinguished. From the scanning electron-microscopic study of an AP single crystal, maintained at 226 °C for two hours, it turned out that the decomposition centres observed in the optical microscope on the *m*-face are holes with shapes corresponding to the *m*-face, while the decomposition centres on the *c*-faces are rhombohedral holes. Both types of holes, and particularly the transition area between the decomposition sites and the unchanged AP, are partially covered with a lid of AP. Around some holes, broken fragments of AP can be observed, indicating that some of the lids popped off during the decomposition. This is probably the reason of the sudden appearance of dark points (decomposition centres) corresponding to the holes under the microscope; this also means that, before the observation of the decomposition centres, a subsurface reaction is taking place. The disk-like centres on the *m*-face and the streak-like ones on the *c*-face grow with the progress of the decomposition, overlap, and finally form a continuous layer of porous AP. After this, the reaction takes place at the interface between the material of porous structure and the undecomposed AP.

The increase in thickness of the porous layer at constant temperature, in vacuum, at atmospheric pressure, and in nitrogen of 35 atmospheres was linear with time in each case. The values of the rate constant were practically independent of the nature and the concentration of decomposition products at the interface and of the pressure of nitrogen. From this latter, KRAEUTLE concluded that the rate-determining step occurs in the condensed phase. The value of the activation energy varied in the range 19.8 to 21.1 kcal/mole.

Since activation energy values of 31—33 kcal/mole were obtained for the growth of the nuclei, and of 20 kcal/mole for the interface decomposition, it was

concluded that the kinetic constants are functions of the particle size and of the number of nuclei developing on the surface of the sample.

The mass-spectrophotometric method was applied fairly recently for the kinetic study of the decomposition of AP. PELLET and SAUNDERS [51] used the $\text{Cl}_2/\text{HClO}_4$ and the Cl_2/Ar ratios for normalization of the decomposition products. The chlorine formation curve taken at 211 °C (Fig. 5) shows clearly the acceleration and deceleratory periods of the decomposition.

The rate constants for the deceleratory period, calculated with the Prout—Tompkins equation, as a function of $1/T$ show a break above 211 °C. Activation energies of 10.4 and 55 kcal/mole were obtained for the low-temperature stage, 157—211 °C, and for the stage 211—232 °C, respectively. These results indicate that, in addition to the temperature ranges mentioned above, there exists an earlier temperature range in which the decomposition of AP differs in characteristics from the others.

The low activation energy values were explained by the authors by the circumstance that in the high vacuum the decomposition of the substance between the strained grains requires a lower activation energy than at higher pressures, because of the easier desorption and diffusion of the decomposition products. The change observed in the activation energy values was explained by a competition between the sublimation and the decomposition, which alters the kinetics of the decomposition process at the temperature corresponding to the breakpoint.

Using a very similar method, GOSHGARIAN and WALTON [47] determined the activation energies for the formation of each individual gas product on the basis of the temperature dependence of the ionic intensities in the range 140—250 °C. They obtained three activation energy values: 22.2, 29.5 and 44.4 kcal/mole.

BOLDYREV *et al.* [56] followed the decomposition of AP by determining of the amount of ClO_2 with an ESR method. The change of the ClO_2/AP ratio as a function of time is shown in Fig. 6. The amount of ClO_2 was merely 1—2% of the perchloric acid formed on dissociation of AP.

The shapes of the curves are completely similar to those of the pressure *vs.* *t* curves for the decomposition of AP. An activation energy of 27 kcal/mole was calculated from the temperature dependence of the rate constants. The authors also investigated the effects on the formation of ClO_2 of copper compounds and of sulfate ions incorporated into the AP. The copper compounds promoted the ClO_2 formation to a large extent, whereas the incorporated sulfate ions exerted a retarding effect.

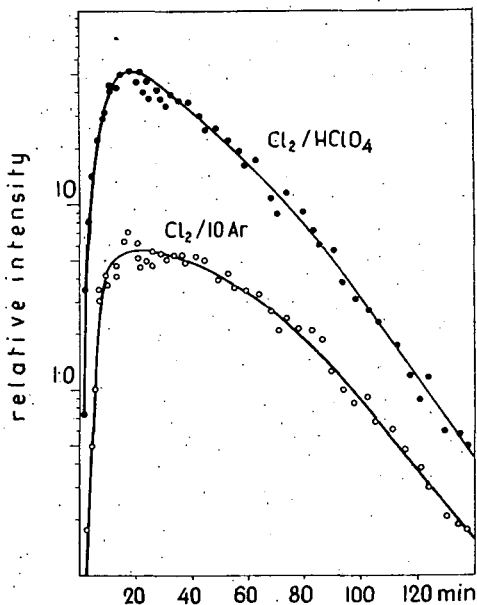


Fig. 5. Relative ion intensity of the Cl_2 formed in the decomposition of AP. Temperature 211 °C (Mass-spectrometric analysis).

Disregarding the abnormal values of the activation energy, it can be stated that (between 200 and 240 °C) the activation energies of the decomposition of the orthorhombic modification and those of the cubic modification lie in the ranges 27–32 and 21–26 kcal/mole, respectively.

The results of the kinetic investigations clearly show that the decomposition of AP changes at about the temperature of the crystallographic transition. BIRCUMSHAW

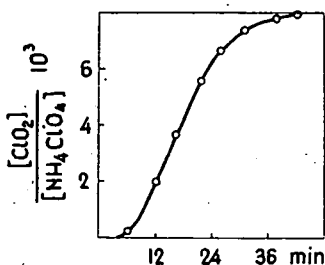


Fig. 6. Amount of ClO_2 formed in the decomposition of AP. Temperature 290 °C (ESR measurements)

and NEWMAN [38] found that the rate of decomposition decreases above 240 °C and attains a minimum at 250 °C. The phenomenon was explained by the decrease of the lattice dimensions, which reduces the number of interstitial ammonium ions. As a possible explanation a slow phase-change may also be taken into consideration, as well as the fact that the cubic modification is the most stable at 240 °C.

MARKOVITZ and BORYTA [2], however, observed an increase in crystal volume at the transitional point, which contradicts the above interpretation. On the basis of most recent crystal diffraction studies, the decrease of the decomposition rate at about 240 °C is explained by supposing that, in addition to the reversible, first-order modification change, a second-order

irreversible transition also occurs somewhat below 240 °C, and in contrast with the first-order process, this is not instantaneous [86].

According to MANELIS and RUBTSOV [87], the phase transition affects the rate of development of the reaction centres, and leaves the number of electron traps responsible for the decomposition unchanged. Accordingly, the lower reactivity is brought about by the increase in crystal volume by decreasing the rate of formation of the reaction centres.

Kinetic investigation of the high-temperature decomposition

Concerning the high-temperature decomposition of AP fewer kinetic investigations have been carried out than in the previous case. The first kinetic work was reported by BIRCUMSHAW and NEWMAN [80]. The measurements were made at 380–450 °C, the pressure being determined in the presence of 40 torr nitrogen, to reduce the extent of sublimation. The decomposition was of a deceleratory character throughout. Rate constants were evaluated with the equation

$$p = kt^n \quad (15)$$

The value of n increased with the increase of temperature. The activation energy was not calculated.

More detailed kinetic measurements were made between 400 and 440 °C with the thermogravimetric method [93]. The rate constants were obtained from

$$m^{2/3} = -kt + \text{constant}, \quad (16)$$

where m is the weight of undecomposed AP at time t . The value of the rate constant

increased proportionally to the increase of the nitrogen pressure ($\sim p_{N_2}^{0.6}$). The activation energy was found to be 73.4 kcal/mole. Reproducible results were not obtained in the range 300 to 380 °C.

In extensive kinetic investigations, GALWEY and JACOBS [94] evaluated the α vs. t curves with the contracting cube formula

$$1 - (1 - \alpha)^{1/3} = kt. \quad (17)$$

From the temperature dependence of the rate constants, a value of 38.8 kcal/mole was obtained for the activation energy of the reaction, and this value was reproduced later by other authors [95]. A nearly similar activation energy was also obtained on the basis of measurements of the amount of gases formed at atmospheric pressure [89].

A significantly smaller activation energy (30.6 kcal/mole), however, was reported in the recent work of JACOBS [96] for the temperature range 287 to 375 °C.

The measurements of OSADA and SAKAMOTO [40] indicated that the activation energy of the high-temperature decomposition varied to a larger extent (between 31 and 46 kcal/mole) with the grain size than in the low-temperature stage.

The thermal decomposition of AP, partially decomposed at low temperature, was studied at high temperature by SHIDLOWSKI *et al.* [91]. The residue of the low temperature decomposition decomposed with a considerably higher activation energy than the original substance. The higher activation energy of the partially decomposed AP can be explained by the loss of reaction sites particularly favourable for the decomposition and by the lower reactivity of the residual substance. Unfortunately the kinetic data of this work must be accepted with reserve, since the reaction of deceleratory nature was evaluated with the Avrami—Erofeyev equation derived for autocatalytic decompositions.

The decomposition of AP was investigated by WAESCHE and VENOGRAĐ [97] with a differential scanning calorimeter. In the kinetic analysis of their measurements they assumed first-order kinetics. They used the following formula for their calculations:

$$\frac{D_T}{(1 - \infty_T)W_0} = k_T q \quad (18)$$

where D_T is the rate of heat evolution at temperature T ; $W_T = (1 - \infty_T)$; W_0 is the weight of the sample at temperature T , and q is the total reaction heat. Activation energies of 61.1 and 30 kcal/mole were calculated for the temperature ranges 400—450 °C and 300—340 °C, respectively. The increase of the pressure between 1 and 30 atm shifted the second exothermic peak of the decomposition towards lower temperatures. The grain size and the origin of the sample did not exert substantial effects on the position of the second exothermic peak.

Effects of the decomposition products on the decomposition of AP

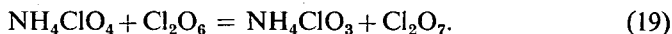
For establishing the mechanism of decomposition of AP, the knowledge of the effects of the decomposition products is of fundamental importance. It was BIRCUMSHAW and NEWMAN [38] who first observed that the induction period of the reaction at 230 °C is significantly increased by ammonia, which in addition reduces the rate and extent of the reaction. Later, more detailed studies showed that ammonia

exerts an inhibiting effect on both the low and the high-temperature decompositions [78, 98, 99].

Only very few experiments have been carried out on the effect of perchloric acid, in spite of the assumption that it plays a great role in the course of the decomposition. Preliminary addition of perchloric acid to AP (HClO_4 : AP = 1:50 w/w) decreased the induction period of the decomposition at 230 °C [38]. The DTA experiments of OSADO and SAKAMOTO [40] showed that in the presence of a few drops of perchloric acid the substance completely decomposed at 250 °C. It was observed that the rate of the low-temperature decomposition increased by a factor of three when one drop of 60% HClO_4 was added to a 50 mg AP tablet [79].

An important effect is also exerted on the decomposition of AP by water. Microscopic studies indicate that in the presence of water the growth rate of the nuclei is also anisotropic. In low concentrations, water decreases the rate of growth of the nuclei, while with increasing water concentration the rate increases to a maximum and decreases again.

The experiments of SVETLOV and KOROBAN [100] indicate the inhibiting effects of the decomposition products, and primarily of water. They showed that the extent of the decomposition depends on the ratio of the size of the AP sample and the volume of the reaction vessel. At a given temperature the decomposition of AP proceeds until a definite pressure is attained. An important role was attributed to the reaction between AP and the Cl_2O_6 formed by the decomposition of perchloric acid

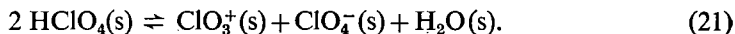


On this basis, the action of water was ascribed to the reaction



In the experiments of WISE [99], 500 torr water at 275 °C decreased the maximum rate of the decomposition to $1/3$, and its extent to $1/2$. The interesting observation was made that, in contrast with the uncatalysed decomposition, ammonia did not inhibit the catalytic reaction.

The inhibiting effect of water was explained by the reversal of the reaction



Few experiments have been reported on the effects of other decomposition products of AP. SCHMIDT [98] observed that at 280 °C hydrogen chloride and chlorine accelerate the decomposition up to 30% conversion. In the presence of chlorine the decomposition proceeds up to 100%. The induction period is not affected by these gases.

The effects of various inert or reactive gases on the ratio of the products formed in the gas-phase decomposition of AP were studied by MAYER and SMITH [57] with mass-spectrometric analysis. In the presence of inert gas the maximum yield of ClO_2 was increased and occurred at higher temperatures. The formation of the gaseous products (HCl , O_2 , NO_2 , ClO_2 , Cl_2 and HClO) was affected to a large extent by preliminary addition of NO to the gaseous AP. The effect depended sensitively on the partial pressure of NO . In the presence of NH_3 , the amounts of all products except NH_2Cl decreased.

Sublimation of AP

Sublimation of AP occurs parallel with decomposition. Nitrate, nitrite and hydrogen ions were found in the sublimate. Sublimation increases with increasing temperature and decreasing pressure. Inert gases at higher pressure suppress the sublimation, and promote the decomposition of AP. Similarly, the sublimation comes into prominence with the progress of the low-temperature decomposition, after 20–30% reaction.

In the first study in vacuum at 260–320 °C [93], the sublimation rate constant was calculated with the equation

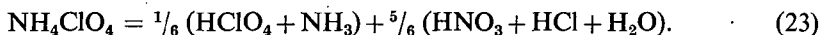
$$\frac{dm}{dt} = k. \quad (22)$$

An activation energy of 21.5 kcal/mole was given for the process. The sublimation was described by the occurrence of the proton-transfer process, by the diffusion of the ammonia and perchloric acid formed, and by their condensation on the cold surface. The influence of pressure was explained by its inhibiting effect on the diffusion process.

Since the activation energy values obtained for the high-temperature decomposition of AP were considerably higher than the activation energy of sublimation, GALWEY and JACOBS [94] concluded that decomposition and sublimation are competitive processes which proceed by different mechanisms. They assumed that sublimation includes the evaporation of an ion-pair. The ion-pair was attributed to the proton-donating property of perchloric acid and the stabilizing effect of the hydrogen bond. The dissociation of the AP was considered unlikely because of the strongly acidic character of perchloric acid.

Numerous experiments have been performed to prove or disprove the above sublimation mechanism and the existence of the ion-pair. According to a linear pyrolysis study, the extent of dissociation in the sublimation equilibrium is limited. A value of 25 kcal/mole was obtained for the heat of sublimation [101].

However, CASSEL and LIEBMAN [102] found that one sixth of the sublimation is simple dissociation to ammonia and perchloric acid, while in the remaining five sixths nitric acid, hydrogen chloride and water are formed. The overall process is symbolized by the following equation:



A decisive evidence for the dissociative sublimation



was provided by the measurement of the dissociation pressure of AP, and also by the inhibitive effect of ammonia [34]. AP pretreated at low temperature was used, and the dissociation pressure was calculated by determining the NH_4^+ and ClO_4^- ions in the sublimate at 237–347 °C. For the dissociation pressure the relation

$$\log P(\text{mm}) = \frac{6283.7}{T} + 10.56 \quad (25)$$

was obtained. A value of 58 ± 2 kcal/mole was calculated for the heat of dissociation.

It was established that, parallel with the evaporation, also decomposition of AP occurs, but this process does not affect the dissociation of AP. In the sublimate 2—3 mole% Cl^- ion was also found. The presence of ammonia in the helium carrier gas completely suppressed the dissociation of AP. The sublimate contained also ammonium chloride which was ascribed to the interaction of ammonia and chlorine formed in the decomposition



Direct evidence against the sublimation *via* evaporation of the ion-pair, and for the dissociative sublimation, was provided by matrix isolation method combined with infrared analysis [103, 104] and mass-spectrographic [46, 48, 52—54, 57] investigations. In the elucidation of the problem, the first method provides the advantage that the substances formed on evaporation are immediately frozen out in the inert gas, and so their further reaction is eliminated. This procedure is also suitable for the detection of weakly bonded complexes, which dissociate as a result of electronic impact in the mass-spectrophotometer. Studies with both methods support the dissociative sublimation; an AP ion-pair was not detected.

The kinetics of the sublimation was recently studied in detail by JACOBS *et al.* [79, 96] at 304—375 °C at atmospheric pressure and in vacuum. They used AP samples which had been decomposed to about 30%. The most suitable equation for the calculation of the rate constant at atmospheric pressure was found to be

$$1 - (1 - \alpha)^{1/3} = kt. \quad (27)$$

The rate constant proved to be independent of the origin of the AP and its grade of purity, but it decreased with increasing the amount of the sample. The value of the activation energy was 28.04 and 30.6 kcal/mole, respectively.

The rate of sublimation in vacuum was described by the equation

$$1 - (1 - \alpha)^{1/2} = kt \quad (28)$$

up to $\alpha = 0.9$. The activation energy was found to be 30.0 kcal/mole, which is exactly the half of the experimentally and theoretically determined value of the enthalpy of sublimation.

It must be mentioned, however, that a number of investigations have resulted in values differing from $\frac{1}{2}\Delta H$ (~ 30 kcal/mole) for the activation energy of sublimation. Thus, PELLETT and SAUNDERS [51] obtained an activation energy of 21 kcal/mole for the formation of perchloric acid, which agreed with the value measured by BIRCUMSHAW.

Activation energy values of about 20 kcal/mole were found for the high-temperature sublimation of AP (above 470 °C) with the linear pyrolysis method [105—114], while at 415—475 °C the value was 60 kcal/mole [108]. One of the reasons for an activation energy less than $\frac{1}{2}\Delta H$ may be that in these studies the diffusion does not play an essential role. The particularly high activation energy value obtained at lower temperatures remains an open question, and it cannot be excluded that this is partly due to shortcomings of the linear pyrolysis method, which has been the subject of criticism from time to time.

The rate of sublimation is extremely sensitive to the gas pressure in the reaction vessel [96]. When the total pressure at 270 °C was increased with nitrogen from the

equilibrium pressure of AP to 1 atmosphere, the sublimation rate became about 200 times lower. Setting out from the theoretical considerations of FUCHS [115], and taking into account the surface diffusion and the diffusion through the gas phase, an equation was derived which described the measured data satisfactorily in the pressure and temperature ranges studied. Values of 60.8 and 59.2 kcal/mole were obtained for the enthalpy of sublimation at atmospheric pressure and in vacuum, respectively. These values are in good agreement with the values determined or calculated in various ways on the basis of the assumption of dissociative sublimation. It was concluded from the results that the rate-determining step in the sublimation of AP is the diffusion of ammonia and perchloric acid in the gas phase.

Relying on the experimental results of RUSSEL-JONES and JACOBS, GUIRAO and WILLIAMS [116] investigated possible models for the sublimation of AP from a theoretical viewpoint. They showed that the pressure dependence of the sublimation rate can be affected by the low-temperature decomposition.

BOLDYREV *et al.* [56] determined the rate of dissociation of AP to NH_3 and HClO_4 in a mass spectrometer. In the range 260–340 °C the reaction rate was described by the following equation

$$\frac{dr}{dt_{r \rightarrow 0}} = 10^{9.09} \exp(-2.4 \cdot 10^3/RT) \text{ sec}^{-1}. \quad (29)$$

A value of $8 \cdot 10^{-2}$ was obtained for the sublimation coefficient. This is in good agreement with the value estimated by JACOBS and RUSSEL-JONES, and supports the dissociative sublimation of AP.

The rate-determining step and the mechanism of the decomposition of AP

In the elucidation of the mechanism of the decomposition of AP, the work of BIRCUMSHAW and NEWMAN [38, 80, 93] can be regarded as fundamental. Although the first conceptions as to the decomposition of AP were modified by later studies, and particularly by the results of JACOBS *et al.*, in several respects, it is without doubt that the papers referred to and the ideas described decisively determined the work of other authors. According to BIRCUMSHAW and NEWMAN [80], three different processes can play a decisive role in the decomposition of AP:

(i) An electron-transfer process. This is the transfer of an electron from the perchlorate anion to the ammonium cation.

(ii) A proton-transfer reaction. This is accompanied by the formation of perchloric acid and ammonia.

(iii) The thermal break-down of the perchlorate anion.

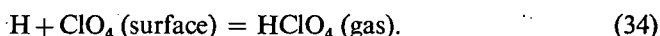
On the basis of the experimental results described above, BIRCUMSHAW and NEWMAN assumed that at 200–300 °C AP decomposes by electron-transfer mechanism.

The electron-transfer process takes place between the perchlorate anion and the ammonium ion in the interstitial sites



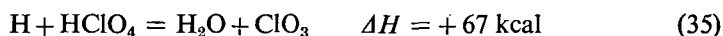
As a result of the stabilizing effect of the crystal field, the perchlorate radical formed cannot break up inside of the crystal; this can take place only if it migrates to the surface. The point of the surface where the perchlorate radical is formed possesses a positive charge. This positive charge can be neutralized either by an electron from the interior of the crystal, or by the diffusion of an ammonium ion to that point from an adjacent position.

The H atoms formed in the process can diffuse to the surface and pass into the gas phase, or they can react with the perchlorate radicals inside or on the surface of the crystal, to form perchloric acid



This reaction-path way does not lead to decomposition, but, because the diffusion of the perchloric acid to the surface is slower than that of the ammonia, it can cause the observed acidity of the partially decomposed substance.

Decomposition can result, on the other hand, if the hydrogen atom reacts with the perchloric acid



with the formation of a chlorate radical which, as an effective electron trap, promotes the increase of the decomposition rate. The authors ascribed the catalytic action of the perchloric acid to the above reaction. The inhibiting effect of ammonia was explained by assuming that reactions (30) and (31) are reversible, and hence the ammonia decreases the formation of the perchlorate radical and reacts with the free perchloric acid.

GALWEY and JACOBS [84] came also to the conclusion that the rate-determining process in the low-temperature decomposition of AP is the electron-transfer reaction. From the consideration that the electron-transfer from the anion to the cation in the ionic crystals corresponds to the excitation of the electron from the valence band to the conductivity band, the activation energy necessary for the electron-transfer process could be calculated from optical data [117]. This activation energy was found to be 35 kcal/mole, *i.e.* only a few kcal/mole higher than the activation energy value determined from kinetic measurements (~ 32 kcal/mole). The agreement of these values was used as evidence for the validity of the electron-transfer process. In contrast with the above, GALWEY and JACOBS assumed that the first process in the decomposition of AP is the formation of an AP molecular complex. The decomposition of this molecular complex constitutes the further reaction steps; decomposition of the isolated perchlorate and ammonium radicals was regarded as much less probable. The rate-determining step in the formation of the nuclei was considered to be the formation of the perchlorate radical, *i.e.* of the positive hole, while in the growth of the nuclei the decomposition of the molecular complex was considered as rate-determining. The first step in the decomposition of the molecular complex is the removal of water, leaving behind nitrogen atoms and chlorine dioxide. Since chlorine dioxide was found among the decomposition products, it

was assumed that the decomposition of chlorine dioxide is fairly slow and is not complete in the reaction zone.

The electron transfer model has been generally accepted for the time being and has been applied to describe the behaviour of AP under different conditions. Support was provided for this mechanism by the significant effects of γ and X-ray radiation on the stability of AP [67—69], and by the changed reactivity of doped AP [30]. This mechanism was used to explain the large catalytic effects of impurities of an electron-acceptor character [118] and semiconducting oxides [44, 45, 119—128].

On the other hand, SCHULTZ and DEKKER [129] evaluating the kinetic data of BIRCUMSHAW and NEWMAN [80] on the basis of transition state theory, pointed out that, even at 200—300 °C, an essential part in the decomposition of AP is played by the proton-transfer reaction. The next stages of the decomposition consist in the splitting off the weakly bonded complex, $\text{NH}_3 \cdot \text{HClO}_4$ from the "interface" and in the gas-phase reaction between ammonia and perchloric acid.

The elucidation of the cause of the cessation of the reaction after 30% conversion in the low temperature decomposition was one of the greatest problems and seemed to be of fundamental importance. To explain the phenomenon it was assumed that the decomposition of the AP was restricted to the substance between the strained mosaic blocks, and that the reaction could not penetrate into the interior of the mosaic blocks [38, 80, 84, 129]. A certain degree of continuity in the solid substance is necessary for the low-temperature solid-phase decomposition, and this does not exist in the residue which has a porous structure. This is supported by the higher activation energy values obtained for the decomposition of the residual material. The poisoning effect of the reaction products as a possible explanation was then rejected.

Since the activation energy of the high-temperature decomposition differed considerably from the low-temperature one, it was justified to assume that the mechanism of the decomposition is different, too. BIRCUMSHAW and PHILLIPS calculated an activation energy of 73.4 kcal/mole at 400 and 445 °C [93].

The authors did consider the possibility of the proton-transfer process, but they finally came to the conclusion that the rate-determining process in this stage is the splitting of the Cl—O bond. Evidence was provided by the fact that this process is also the rate-determining step in the decomposition of the alkali perchlorates, and the activation energy of this decomposition is very close to that of the decomposition of AP.

GALWEY and JACOBS [94] calculated an activation energy of 38.8 kcal/mole from kinetic studies at high temperature. In their view, the rate-determining process is the proton-transfer reaction, and this is followed by the oxidation of the gaseous ammonia by the decomposition products of the perchloric acid. They assumed that the sublimation takes place *via* evaporation of the ion-pair and that the sublimation of AP and its high-temperature decomposition proceed by different mechanisms.

The results of recent investigations further refined this picture and fundamentally modified it in some respects. From this point of view, the following new results can be considered as most important:

1. The activation energy value of 35 kcal/mole calculated from optical data for the electron-transfer from the perchlorate ion to the ammonium ion [84] can be regarded as incorrect. The low-frequency dielectric constant of AP is 5.1 [32], and its

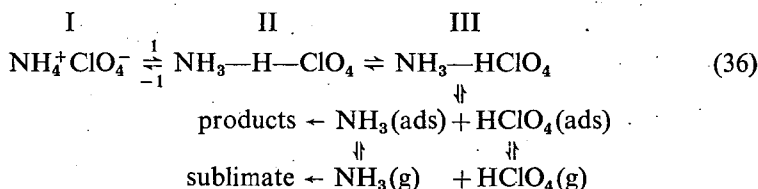
absorption edge is at 2040 Å [30]. Taking into account the refractive index of AP, a value of 60 kcal/mole arises for the thermal activation energy.

2. Mass-spectrographic studies did not confirm the existence of the molecular complex of AP but, in contrast, indicated the formation of ammonia and perchloric acid.

3. A study of the vapour pressure, sublimation and heat of evaporation of AP clearly supported the dissociative evaporation of AP.

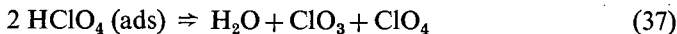
4. It emerged from a study of the gas-phase decomposition of perchloric acid that this is substantially more stable than previously thought [130].

In the knowledge of all these experimental findings and on the basis of more recent kinetic data (the activation energies of the low and high-temperature decompositions and also the sublimation of AP are identical, 30 kcal/mole), RUSSEL—JONES and JACOBS [79] assumed that all these processes take place by the proton-transfer mechanism, according to the following reaction scheme:



(I. An AP ion-pair at the half-crystal site; II. the transition state; III. the completion of the proton-transfer process).

At low temperature, where the decomposition is faster than the sublimation, the NH_3 and HClO_4 remain adsorbed on the solid AP surface and decompose there or react with each other. The HClO_4 presumably decomposes in a bimolecular process



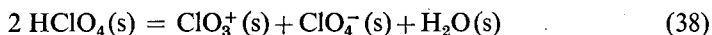
The adsorbed NH_3 is oxidized by atomic oxygen formed in the decomposition of the unstable chlorine oxides, or by the chlorine oxides themselves.

It is assumed that the adsorbed HClO_4 is more rapidly desorbed than the NH_3 , or the oxidation of adsorbed ammonia is not complete, and thus, with the progress of the reaction, the surface becomes saturated with ammonia; this leads to the suppression of the dissociation process. The authors considered that this causes the ceasing of the low-temperature decomposition of AP after 30% conversion. In agreement with the above are the observations that on introduction of ammonia the extent of the decomposition further decreases, although in our opinion the explanation given by BIRCUMSHAW for the inhibiting action of ammonia cannot be completely excluded.

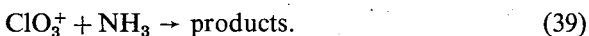
With increasing temperature, above 300 °C, the dissociation process becomes more dominant and instead of reacting on the surface the NH_3 and HClO_4 formed desorb [79]. At low gas pressure they rapidly diffuse out of the hot zone and recombine on the cold parts of the reaction vessel (sublimation). However, at the same time, the decomposition of HClO_4 takes place and the oxidation of NH_3 also begins (decomposition). With the decrease of the rate of diffusion on applying higher gas pressure, the latter process comes into prominence.

The fact that the sublimation (*i.e.* the proton-transfer process) continues after the cessation of the low-temperature decomposition shows that the adsorbed NH_3 is not able to suppress the dissociation process. JACOBS explains this feature by assuming that with the suppressing of the dissociation process the surface HClO_4 concentration decreases to such an extent that desorption occurs instead of the bimolecular decomposition of HClO_4 .

According to WISE [99], the decomposition of the perchloric acid formed in the proton-transfer process, similarly to that of nitric acid, gives ionic products



and the ammonia is oxidized by the ClO_3^+



The above transformation of the perchloric acid explains the inhibiting effect of the water. In his opinion, this reaction step, which is decisive for the decomposition, presumably takes place only on suitable defect sites of the AP crystal, since after 30% conversion the decomposition ceases, while the dissociative evaporation of AP continues.

Because of the sublimation of the residual AP, WISE still explains the cessation of the decomposition of AP with the original BIRCUMSHAW model.

MAYCOCK and PAI VERNEKER [30], on the basis of the strong relation found between the rate of decomposition and the conductivity of AP, as well as of the reactivity of doped AP, consider the above reaction mechanism proposed by JACOBS as oversimplified. They explain the 30 and 100% decompositions with different reaction mechanisms and with different defect-structures of the crystal. In their view, below 250 °C the electron-transfer mechanism for AP is still the dominant one, and this requires the formation of fresh surfaces. The formation of Frenkel-type defects, however, does not result in new surfaces, and as a consequence, the decomposition comes to a halt. Above 300 °C the AP contains Schottky defects, the formation of which is accompanied by the production of a new surface, and so the decomposition continues to 100%.

Fairly recently, JACOBS and PEARSON [131] described a detailed mechanism for the decomposition of AP by taking into consideration the known decomposition products and the available thermochemical data. They dealt more exhaustively with the high-temperature reaction, but in their view the same reaction steps are valid for the low-temperature decomposition, too.

At high temperatures, above 315 °C, the homogeneous-phase decomposition of the HClO_4 formed in the process of dissociation of the AP takes place in accordance with the reaction



The rate-determining step is the splitting of the Cl—O bond. The experimentally obtained activation energy is 45.1 kcal/mole, in good agreement with the energy of dissociation of the Cl—O, 47.6 kcal/mole, in the HClO_4 .

In the subsequent reaction steps, ClO_2 , ClO and atomic and molecular oxygen are formed. The ammonia may be oxidized by any of the decomposition products of the perchloric acid. Earlier, the oxidation was described with atomic oxygen, since the reaction with molecular oxygen in the absence of catalysts is extremely

slow. The oxidation with atomic oxygen, on the other hand, also gives hydrogen, but the formation of N_2O is excluded, and this constitutes a fundamental difference compared with the distribution of products found in the decomposition of AP.

Recent considerations regard ClO as the most important oxidizing radical which is formed in the decomposition of ClO_3



The reaction of ClO_3 leading to the formation of ClO_2



is an extremely endothermic process, and so it is thermodynamically less probable. The formation of ClO_2 in the heterogeneous-phase decomposition of perchloric acid



however, is a less endothermic process. The ClO_2 formed in the decomposition of AP can react with atomic oxygen and with atomic chlorine



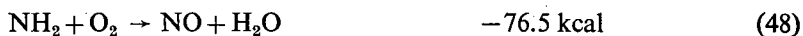
Its decomposition is about five times faster than the chlorine-catalyzed recombination of oxygen atoms.

Confirmation is still needed for the assumption that ClO_2 does not form, or accumulate on the decomposition of ClO_3 , and that it is produced only on the heterogeneous-phase decomposition of $HClO_4$.

For the oxidation of NH_3 the following reaction steps are proposed:



or



or



This latter, however, is not probable because of the value of the reaction heat.

The regeneration of ClO can take place in the following processes:



and its termination in the reaction



The ClOO decomposes rapidly by the steps



The most probable way for the formation of N_2O is



or



In addition to the above, the HNO can still be transformed in the reactions



NO_2 can also be formed in the processes



The molecular oxidation of NO is not probable at the temperature of the decomposition of AP, since the equilibrium is displaced in the direction of the formation of NO.

Explosion of AP

At atmospheric pressure AP explodes at 430—450 °C [101]. This temperature value is usually termed the minimum explosion, or ignition temperature.

The explosion of AP is of thermal origin; the increase of the temperature of a sample during the rapid decomposition leading to the explosion can be measured with the aid of a thin thermo-element. At the instant of the explosion a flash of light can be observed, and the gas is liberated immediately.

Using 50 mg powdered AP at 440—530 °C in air at atmospheric pressure, GALWEY and JACOBS [101] obtained an activation energy of 41.5 kcal/mole for the reaction leading to the explosion. They assumed that the proton-transfer process plays a decisive role in the explosion of AP.

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СТРУКТУРА И ТЕРМИЧЕСКОЕ РАЗЛОЖЕНИЕ ПЕРХЛОРАТА АММОНИЯ

Ф. Шоймоши

Работа даёт подробную информацию, путём критической разработки литературных данных, о структуре перхлората аммония, экспериментальных методах изучения его термического разложения, кинетике и механизме разложения.