

MECHANISM OF THE CATALYTIC DECOMPOSITION OF AMMONIUM PERCHLORATE

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A critical survey on the various interpretations suggested for the effect of different additives on the thermal decomposition and ignition of ammonium perchlorate is given. On the basis of all the data and observations, a mechanism for the catalytic decomposition of ammonium perchlorate is proposed.

In the previous paper we summarized the main results of kinetic and thermal analytical measurements concerning the effect of oxides and different salts on the slow and fast decomposition of ammonium perchlorate (AP) [1]. In the present review we examine first the influence of catalysts on the gas-phase decomposition of AP, and collect all the data regarding the interaction between catalysts and AP, and then give a critical survey on the various interpretations proposed for the effect of additives on the stability of AP.

Finally, on the basis of all the data and informations we attempt to derive the most probable mechanism for the catalytic decomposition of AP.

Catalysis of the gas phase decomposition of AP

The first experiments on the catalysis of the gas phase decomposition of AP were reported by HERMONI and SALMON [2]. According to the brief conference abstract, chromic oxide and copper oxide are able to catalyse the gas phase reaction of AP.

In the more detailed experiments of BOLDYREV *et al.* [3] the AP was separated from oxides by glass wool. It was found that the rate of the gas phase decomposition of AP is increased by many oxides, but data were reported only for the effect of NiO (Fig. 1).

In the presence of nickel oxide the pressure of permanent gases increased, the effect being the greater, the larger the surface of the oxide. Since the decomposition of AP occurred under the reaction conditions used also in the absence of the catalyst, it could not be excluded that the oxides affected the secondary reactions between the products in such a way that the pressure of the permanent gases increased.

Experiments convincing with regard to the catalysis of the gas phase reaction were those made with 30% decomposed AP, the oxides being placed on sintered glass above the AP residue after the reaction [4, 5]. As can be seen from the few measurements in Fig. 2, decomposition of the pure AP was extremely small or

negligible in this case, and the observed pressure increase was due exclusively to the catalytic decomposition of vaporized AP.

In general, transition metal oxides catalysing also the low temperature decomposition of AP proved to be effective. ZnO, however, exhibited a strikingly high catalytic activity; even at 260°C it accelerated the gas phase decomposition of AP to a large extent. For comparison, the effects of some oxides on both the slow decomposition of AP and the lowest temperature of ignition were studied.

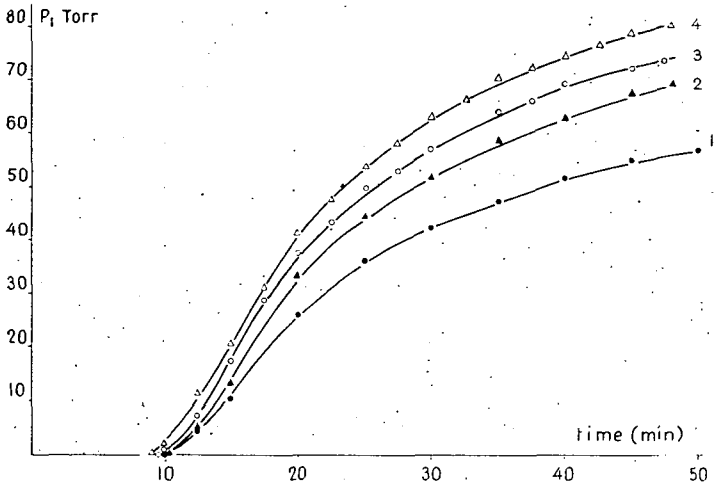


Fig. 1. Gas-phase decomposition of AP on nickel oxide of different surface area. 1: pure AP; 2: NiO 2 m²/g; 3: NiO 5.4 m²/g; 4: NiO 36 m²/g

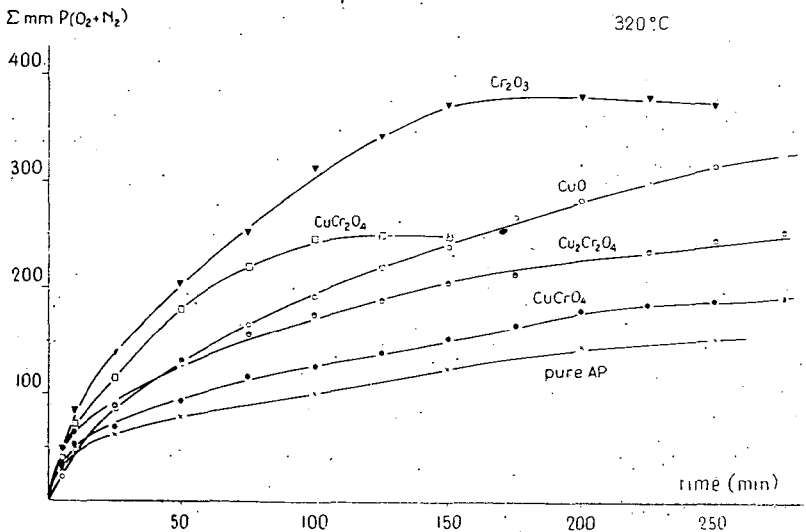


Fig. 2. Gas-phase decomposition of AP on different oxides

According to the typical data in Table I, the series of effectiveness of the oxides is fairly different in the low temperature decomposition from that in the high temperature decomposition; this permits conclusions on the change of importance of the individual reaction steps. Nor was there a close connection between the effects of the oxides exerted on the decompositions of perchloric acid and of AP (Tables I and IV).

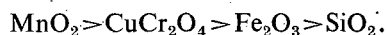
Table I

Effect of oxides on the slow decomposition, the ignition, and the gas-phase decomposition of AP; mole ratio of the AP:oxide mixture 10:1

Catalyst	Slope of $p-t$ curves, 225°C	Minimum ignition temp., °C	t_0 , at 320°C
ZnO	1.71	252	6.1
MgO	1.04	280	42.0
Cu ₂ O	0.795	256	—
CdO	0.692	268	—
NiO	0.650	263	18.0
CoO	0.592	261	20.5
CuO	0.487	264	16.0
Fe ₂ O ₃	0.319	307	28.5
TiO ₂	0.303	385	43.5
Cr ₂ O ₃	0.300	293	13.3
SnO ₂	0.287	390	53.0
CrO _{1.97}	0.262	270	—
Al ₂ O ₃	0.257	385	35.0
CaO	0.190	360	—
Without catalyst	0.250	420	57.0

t_0 = time (in minutes) for 50% decomposition

BOLDYREV *et al.* [6] recently investigated the gas phase decomposition of AP on manganese dioxide, copper chromite, iron(III) oxide and silica. The activities of the oxides decrease according to the following sequence:



It was shown that in the presence of ammonia the decomposition of perchloric acid increased to about the 10-fold; this was explained by the re-establishment of the original state of the catalyst oxidized by the perchloric acid.

In their view, the order of effectiveness of the oxides is the same in the decompositions of both AP and perchloric acid; from this, conclusions were drawn on the importance of the catalytic decomposition of perchloric acid in the decomposition of AP. Since their studies covered only four oxides, their comparison was not sufficiently founded.

Effect of additives on the products of decomposition of AP

Rather few investigations have been reported on the effects of additives on the products of decomposition of AP.

HERMONI and SALMON [7] found that the quantity of oxygen decreased in the presence of nickel, cobalt, manganese and chromic oxides. An increase in the chlorine

dioxide content was reported, but this result was not confirmed by later studies; the increase of the ClO_2 content was attributed to the use of a wrong analytical method [8].

The studies of SHMAGIN and SHIDLOVSKII [9] showed that transition metal oxides decreased the extent of chlorine and dinitrogen oxide formation. The nitrogen was found primarily in the form of NO. These oxides barely affected the formation of HCl. An extremely large decrease of the HCl content was observed only in the presence of zinc oxide.

INAMI, ROSSER and WISE [8] studied the decomposition products of AP in the presence of copper chromite, as well as of cobalt and iron oxides. The products of the catalytic reaction were determined by subtracting the values measured in the decomposition of pure AP from the data found.

The most substantial difference between the products of the two reactions was that N_2O and HCl are not formed in the catalysed reaction. The results of the chemical analyses are reported in Table II.

Table II

Products of decomposition of ammonium perchlorate in the presence of Harshaw CuCr_2O_4

Temp. (°C)	Conc. (Wt %)	Yield							Recovery		
		O_2	N_2	N_2O	Cl_2	HNO_3	HCl	NO	N (atom%)	Cl (atom%)	Wt % decomp.
250	0	0.61	0.055	0.37	0.39	0.14	0.15	0.006	98.7	93.4	19.8
250	1.79	0.54	0.064	0.32	0.45	0.15	0.091	0.019	93.8	100.2	29.4
250	3.99	0.54	0.078	0.30	0.43	0.15	0.11	0.026	93.6	100.0	31.0
275	0	0.55	0.051	0.36	0.39	0.15	0.17	0.011	97.8	96.0	26.8
275	0	0.50	0.047	0.35	0.39	0.19	0.16	0.019	99.1	94.9	26.5
275	1.03	0.56	0.073	0.29	0.41	0.17	0.12	0.014	91.7	94.7	35.3
275	1.79	0.47	0.080	0.28	0.44	0.20	0.095	0.023	94.9	99.4	36.5
275	2.73	0.47	0.090	0.26	0.44	0.20	0.10	0.026	92.9	100.9	36.2
275	3.90	0.53	0.12	0.25	0.42	0.22	0.10	0.024	97.6	96.8	38.7

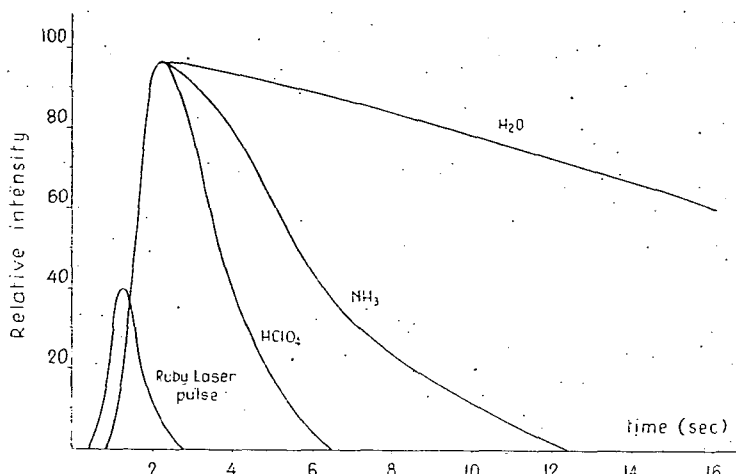


Fig. 3. Evolution history of the products in laser pyrolysis of a mixture of AP: Fe_2O_3 (5 w%)

PELLETT and SAUNDERS [10] studied the effects of iron oxide, copper chromite and manganese dioxide on the decomposition products of AP with a time-of-flight mass-spectrometer. The AP was heated up rapidly with a diamond laser. It was assumed that the decomposition products were formed in the heterogeneous phase reaction at high temperature (500–600°C). The first step was the dissociation of AP to ammonia and perchloric acid. The latter decomposes rapidly on the surface of the solid, the main products being chlorine dioxide and hydrogen chloride. A fairly slight decomposition of the chlorine dioxide was also observed; in high vacuum, under the experimental conditions, its stability exceeded that of perchloric acid. NO also occurred as a main product. The sequence for the amounts of nitrogen compounds formed was:



Fig. 3 shows the time dependence of the primary products in the presence of iron oxide.

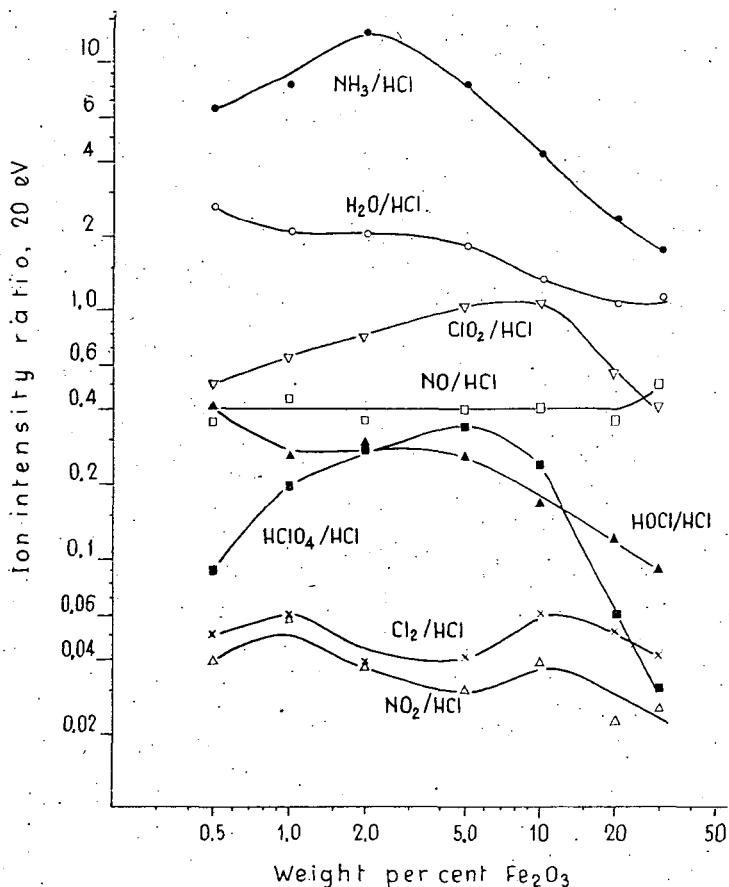


Fig. 4. Laser pyrolysis of AP: Harshaw copper chromite and Fe₂O₃.

In Fig. 4 the product distributions in the presence of copper chromite and iron oxide is presented.

In order to distinguish nitrogen and nitrogen dioxide from carbon monoxide and carbon dioxide, ^{15}N -containing AP was used in some experiments. The relative amounts of products in the presence of various oxides are given in Table III.

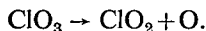
Table III
20 eV product distributions obtained from Laser
pyrolyses of $^{15}\text{NH}_4\text{ClO}_4$ /metal oxide mixtures

Wt % (estimated)	Harshaw Cu 0202	Fe_2O_3	MnO_2
	50	50	70
HCl	1.00	1.00	1.00
N_2	0.20	0.14	0.31
CO	0.2	0.19	0.2
N_2O	0.11	0.04	0.13
CO_2	0.75	0.57	0.45
NO	0.88	0.67	0.40
NO_2	0.08	0.03	0.06
ClO_2	0.72	0.31	1.65
NOCl	0.30	0.09	0.38
$\text{NH}_3 + \text{H}_2\text{O}$	15	3.3	12.3

An important difference in the effects of the oxides appeared in the case of iron oxide, where the amounts of N_2O , ClO_2 and HOCl were significantly smaller than in the other two cases.

The effects of various oxides on the products of the gas phase decomposition of AP were studied by BOLDYREV *et al.* [6] by mass-spectrophotometric analysis. Some measurements were also made with perchloric acid. The data are given in Table IV.

According to their analyses, there is a temperature range in which the perchloric acid decomposes to chlorine dioxide without the formation of chlorine. This is described by the following reactions:



It is clear from the reported data that if ammonia is present in the system, then there is no molecular oxygen among the secondary products of the catalytic decomposition of perchloric acid. In the low temperature decomposition of AP, however, it was found earlier that oxygen is formed; this was explained by a different decomposition of the perchloric acid.

Table IV

Mass-spectrometric analysis of the gas-phase decomposition of AP in the presence of catalysts [6]

Catalysts (m ² /g)	28 N ₂ ⁺ CO ⁺	30 NO ⁺	32 O ₂ ⁺	36 HCl ⁺	44 N ₂ O ⁺ CO ₂ ⁺	46 NO ₂ ⁺	51 ClO ⁺	67 ClO ₂ ⁺	70 ³⁵ Cl ₂ ⁺	72 ^{37,35} Cl ₂ ⁺	83 ClO ₃ ⁺	100 HClO ₄ ⁺	T, °C
MnO ₂ (25)	15	540	54	61	69	108	—	—	230	155	—	—	200
	68	415	83	108	177	77	15	—	346	223	—	—	150
	50	208	50	82	98	46	25	46	216	140	—	—	100
CuO (0.2)	8	100	33	47	55	—	38	63	56	—	1	—	275
	5	16	34	20	25	—	68	78	—	—	27	11	200
Bauxit (30)	13	252	118	59	173	—	36	82	227	—	—	—	330
	39	131	23	46	31	—	62	92	100	—	—	—	300
	40	50	23	46	67	—	70	111	—	—	—	—	260
	19	5	15	19	24	—	56	85	—	—	40	16	210
SiO ₂ (10 ⁻³)	7	7	10	20	17	—	60	113	—	—	43	17	300
	8	6	26	20	20	—	60	109	—	—	51	20	260
	15	—	11	20	14	—	48	111	—	—	72	29	210
Fe ₂ O ₃ (3)	69	120	82	45	71	38	69	106	138	106	10	—	210
CuCl ₂ O ₄ (20)	15	19	71	31	71	13	50	96	79	44	60	27	165

Interaction between AP and the catalyst

As has been seen above, the admixture of oxides to AP essentially changes the direction and products of the decomposition of AP in many cases. As has already been shown in numerous instances in contact catalytic reactions, the products of the catalytic reaction modify the surface composition and physical and chemical properties of the catalyst. It was mentioned above that in the case of copper(I) oxide the catalyst is oxidized to copper(II) oxide [11]. A number of authors have observed a similar oxidation with chromic oxide and copper chromite catalysts [7, 12]. HERMONI and SALMON [2] found the formation of CrO₂Cl₂ at 200—240°C.

It was observed by ROSSER, INAMI and WISE [8, 13] that the copper chromite catalyst was oxidized at 275°C; even at the beginning of the decomposition of AP its colour changed from black to brown, and this was accompanied by the cessation of the catalytic effect. (Under the decomposition conditions cobalt oxide was also oxidized but its catalytic effect did not cease.) An aqueous solution of the catalyst contained chromate ions. The authors assumed that the oxidation of the catalyst is caused by a strongly oxidizing intermediate (chlorine dioxide) formed in the catalytic reaction. It was considered less probable that the oxidation was caused by HClO₄ formed in the dissociation of AP.

However, the first results reported on the oxide-catalysed decomposition of perchloric acid showed that even below 200°C perchloric acid is capable of oxidizing

chromic oxide [14, 15]. Accordingly, it is not necessary to assume the formation of a strong oxidant in the catalytic reaction. Similar observations were published by PEARSON and SUTTON [16] in connection with the copper chromite catalyst. The oxidation by perchloric acid is supported by recent measurements of INAMI and WISE [17] in which the oxidation of the catalyst was also observed when it was not directly in contact with the AP.

Other authors found that chromic oxide is not oxidized in the decomposition of AP at 310°C, and in fact, in the presence of AP the oxidation of Cr_2O_3 by air is inhibited [18]. Oxidation was observed only if the mixture also contained potassium chloride.

A substantially greater change than the above occurs when the catalyst reacts with the AP, and the perchlorate salt formed in the reaction exerts a very large promoting effect. With the oxides, such reactions were observed in the presence of ZnO, CdO, MgO, PbO and CaO [19—24].

The formation of perchlorate salts was also observed in the presence of BaCO_3 and CaCO_3 [25, 26].

Unquestionably, the most probable way of formation of the perchlorate salts is that the perchloric formed in the dissociation of the AP reacts with the additive. However, since the above additives also react with other perchlorate salts when no perchloric acid is present, it cannot be excluded that in the case of AP the process occurs *via* an exchange reaction in the solid phase.

Other studies

In spite of the great number of kinetic investigations, rather few attempts have been made to elucidate the effects of mixing and of different reaction conditions. These data, however, can supply very useful information on the mechanism of the effects exerted by the additives and also on the nature of the solid phase catalytic reactions. The extent of the catalytic effect of an additive oxide, and the question whether the catalytic effect need be considered after the termination of good contact between the AP and the oxide, appeared fundamental.

From the analysis of the decomposition curve of an AP— MnO_2 mixture under high pressure, it appeared that the effect of the MnO_2 extends only up to 4% decomposition owing to the termination of the contact between AP and the oxide. Using a powder mixture, HERMONI and SALMON [7] observed almost 100% decomposition, even at low temperature; in this case the continuous renewal of the contact between the AP and the oxide powders was possible, in contrast with the situation in the tablet.

In the case of AP—CuO, the effect of the compression of the powder mixture on the rate of decomposition was studied in more detail [27]. The experiments were carried out in air. Although the effect of the pressure is fairly complex, it is evident from the measurements that the better contact between the substances, brought about by high pressure, favourably affects the commencement of the decomposition of the AP, the initial reaction, and hence, the explosion of the AP. However, high pressure is disadvantageous in the later stage of decomposition and for the extent of the reaction.

Concerning the effect of the gas pressure (air, oxygen, nitrogen), some measure-

ments were made with regard to the rate of the catalysed reaction and the occurrence of the explosion [28]. The increase in pressure of all three gases increased the catalytic reaction rate and, at a sufficiently high temperature, brought about the explosion of the AP. The hindrance to vaporization of the AP and restriction of the reaction to the solid phase clearly play a role in the gas pressure effect.

In this respect it would seem worth-while to study in detail how the course of the catalysed reaction varies with the partial pressure of ammonia. Wise [8] found that, in contrast to the decomposition of pure AP, the introduction of 2 torr ammonia does not inhibit the catalytic reaction at all.

The significance of the contact in the AP—oxide mixture was established by studying various pre-treatments and interruptions [28]. The pre-treatment at 215°C in air, up to the commencement of decomposition, of an AP—CuO tablet (16:1 molar ratio), compressed at 2700 atm, decreased the induction period of the explosion of the mixture at 270°C by about 50%. A similar effect was also observed in the case of the substance decomposed to 25%. Identical behaviour was found in 1:1 molar mixtures, too.

If the pre-treatment and the subsequent measurements were carried out in vacuum, the decomposition began sooner (16:1 molar ratio), here too. However, the pre-treatment even up to 2% decomposition decreased the rate of decomposition considerably.

The pre-treatment exerted substantially greater effects on AP—ZnO [28] and AP—CdO [22] mixtures. The time up to the explosion of a mixture at 270°C decreased with the increase of the pre-treatment time at 200—220°C. The results concerning cadmium oxide are given in Fig. 5.

If the interruption occurred at the temperature of the explosion, on renewed heating the AP—ZnO or AP—CdO mixture exploded after a time which was shorter by the time of previous heating at this temperature ("memory effect"). The duration of the interruption (5 min—24 hours) was an unimportant factor in this behaviour.

A possible explanation for the phenomenon is that, even at a low temperature during the pre-treatment, reaction between the AP and the oxide begins, resulting in zinc or cadmium perchlorate, which are extremely effective in the decomposition of AP [28, 22]. As a result, at higher temperature, the AP explodes after a substantially shorter time.

It is surprising, however, that this effect also occurred with the AP—CuO mixture, though to a smaller extent [28]. This mixture exploded in air at 270°C after 310 seconds. If the material was taken out of the reaction vessel in different stages of the decomposition preceding the explosion, and replaced after standing for about 15 minutes, then the explosion occurred substantially sooner than in the non-pre-treated tablet. The total time up to the explosion, however, was longer here. On the other hand, if the interruption was made at the end of the acceleration stage of the decomposition preceding the explosion (1:1 molar ratio), then the material did not explode any longer on renewed heating.

This means that in the presence of a larger quantity of copper oxide the decomposition could not accelerate to such an extent and could not produce so much heat that the tablet containing this amount of copper oxide should attain a temperature necessary for explosion.

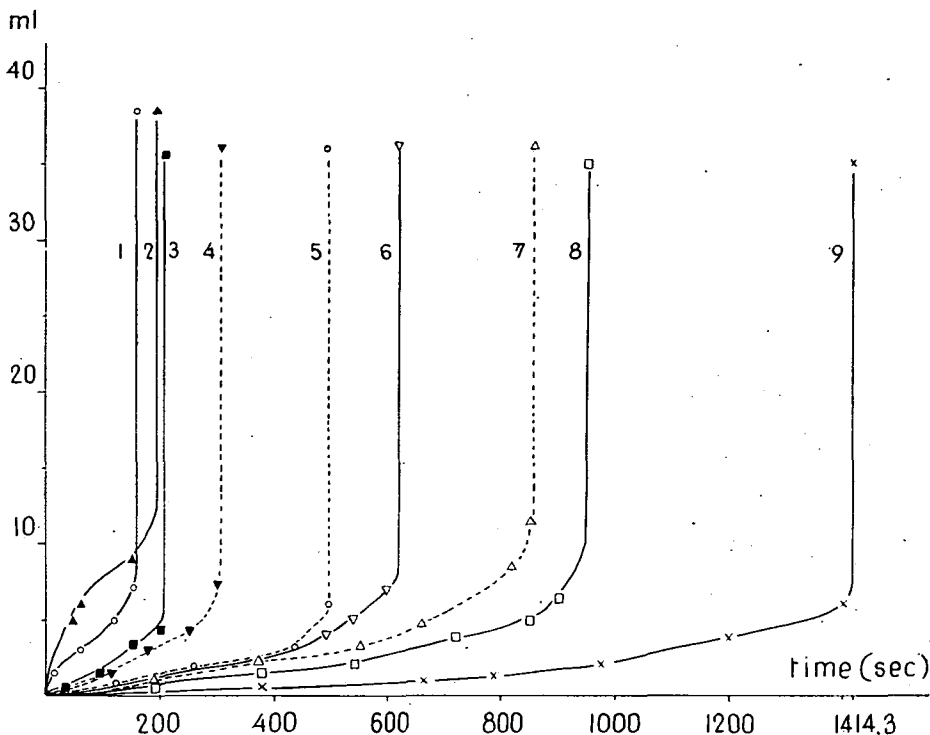


Fig. 5. Effect of low-temperature decomposition on the induction period for ignition of an AP—CdO mixture (mole ratio 10:1) at 285°C. Volume of gases formed *vs.* time. Pre-treatment temperature and time: 1. 200°C, 390 min; 2. 220°C, 240 min; 3. 220°C, 120 min; 4. 200°C, 260 min; 5. 200°C, 160 min; 6. 220°C, 60 min; 7. 200°C, 70 min; 8. 220°C, 20 min; 9. without pre-treatment

Mechanism of the catalytic decomposition of AP

In spite of the large number of studies reported, a generally valid theory of the role of the additives and of the mechanism of the catalytic decomposition of AP has not yet emerged. In the following a detailed account of the different views, their development, applicability and limitations is given.

1. Mechanism of action of oxides

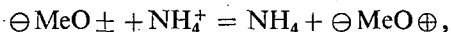
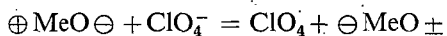
In the derivation of the mechanism of the catalytic reaction, research workers in the overwhelming majority of cases relied on kinetic data, and primarily on the activation energy values. BIRCUMSHAW *et al.* [29, 30] and GALWEY and JACOBS [31, 32] found various activation energy values for the decomposition of pure AP, depending on the temperature region, and ascribed this to different reaction mechanisms. Kinetic studies with pure AP carried out from 1954 to 1962 showed clearly that the low temperature decomposition of AP, below 300°C, occurs by an electron-transfer

reaction. GALWEY and JACOBS [31] presumed that radicals produced in the electron-transfer process form molecular complexes. The decomposition of these complexes takes place in the further reaction steps; the separate, independent decomposition of perchlorate and ammonium radicals was considered less probable. Since the activation energy of the decomposition catalysed by manganese dioxide well approximated the activation energy value ascribed to the electron-transfer mechanism for the decomposition of AP, the action of the oxide was interpreted as the promotion of the electron-transfer process [35]. It was assumed that the AP complex formed after the electron-transfer is stabilized by manganese(IV) ions ($\text{Mn}^{3+}\text{ClO}_4\cdot\text{NH}_4^+$), and the rate of re-formation of the perchlorate ion decreases. The fact that the catalysed and uncatalysed reactions have the same activation energies was explained by the electron-transfer to the catalyst taking place *via* the conductance band of the AP. The effect of iron oxide in the decomposition at 240–300°C was also explained later by the acceleration of the electron-transfer process [34].

From the point of view of elucidating the mechanism of the catalytic reaction and the role of the catalyst, it seemed of fundamental importance to determine which properties of the catalysts are responsible for the catalysis of the decomposition of AP.

According to the view generally accepted earlier, the low temperature decomposition of AP occurs by the electron-transfer process, and the first kinetic studies on the catalytic reaction supported the validity of this reaction [33, 19, 34], therefore, it was rightly assumed [27] that the electrical properties of the oxides may play a decisive part in the coming about of the catalytic action. From this it was expected that the modification of the electrical conductivities of the catalyst oxides should influence their catalytic actions [19, 27, 35]. The systematic investigations carried out from this point of view confirmed this working hypothesis and, on the basis of the available results, led to the conclusion that *p*-type semiconductors are the most effective substances, while *n*-conductors and insulators are substantially less effective or completely inactive [27, 36, 35].

From this it was concluded that the rate-determining process in the catalytic reaction is the first of the following two elementary steps:



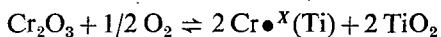
i.e. the formation of the perchlorate radical [27, 35]. Clearly, *p*-type oxides can accelerate only the first reaction. The fact that *n*-conducting oxides (titanium(IV), tin(IV), aluminium(III), molybdenum(VI), tungsten(VI) oxides) are practically ineffective on the decomposition of AP, is in agreement with the proposed reaction mechanism since these oxides of high electron density cannot (or only to a small extent) promote the formation of perchlorate radicals.

Results obtained on doping the semiconductor oxides supported the above picture [27, 35, 37; 38]. From the properties of semiconductor oxides it is known that their conductivities and, therefore, electron and defect-electron concentrations can be increased or decreased by the incorporation of ions of different valency. In the case of *p*-type oxides, the defect-conductance of an oxide is increased by the incorporation of ions of lower valency, while ions of higher valency bring about a decrease of the defect-conductance. The reaction rate of the catalytic decomposition

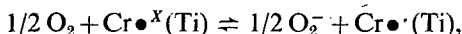
of AP changed with varying the defect-electron densities of the *p*-type copper(II) oxide [27], nickel(II) oxide [37] and chromium(III) oxide [35]. Increase of the defect-electron density increased the catalytic effect of an oxide, and *vice versa*. It is an important result that the catalytic activity of an oxide was modified by doping only if its electrical properties also changed. It could be seen from Fig. 3 of the previous paper [1] that the induction period preceding the explosion of AP was increased by doping the Cr_2O_3 with TiO_2 , while neither ZnO nor NiO additives caused any change. In contrast with TiO_2 , the latter practically did not affect the electrical conductivity of Cr_2O_3 .

In the case of *n*-conducting oxides (TiO_2 or SnO_2), changes in the electron concentration did not bring any essential change; from this it was concluded that, even with the decrease of the electron concentrations (the Fermi potentials of the electrons), the oxides were not capable of promoting the formation of perchlorate radicals. The only exceptions were titanium dioxide [35] or tin dioxide [38] doped with a small amount of chromic oxide.

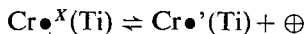
A detailed study of the chromic oxide—titanium dioxide system led to the result that, due to of the oxidation of chromium (valence inductivity) accompanying the incorporation of the chromic oxide,



and further oxygen chemisorption



some of the chromium is converted to valency states four and five [39]. The substitution defects of the $\text{Cr}^{\bullet X}(\text{Ti})$ and $\text{Cr}^{\bullet}(\text{Ti})$ readily dissociate according to the following two equations



and



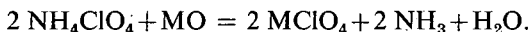
and so defect electrons are formed in a considerable amount. This process occurs primarily in the surface layer of the titanium dioxide where, as a result, an extremely good defect-conductor layer exists. With the assumption of *n*-type \rightarrow *p*-type conversion on the surface, the large catalytic effect of titanium dioxide doped with chromic oxide was explained in an exactly similar way as above [35]. Accordingly, the practically inactive titanium dioxide as a carrier promotes only the formation of a component which is extremely active in the decomposition and explosion of AP. Since the titanium dioxide—chromic oxide mixture has a surplus oxygen content and a surface defect-electron density which considerably exceed those of the same amount of pure chromic oxide, it can be understood on the basis of the above reaction scheme why the effectiveness of the titanium dioxide + chromic oxide surpasses the effect of pure chromic oxide.

Similar processes take place on the incorporation of chromic oxide into the surface layer of *n*-type tin dioxide (formation and stabilization of higher valency chromium ions) [38], and the increased catalytic effect of the tin dioxide doped

with chromic oxide was explained, here too, by the formation of higher valency chromium ions with their large electron affinity.

However, the fact that a significant catalytic effect was observed in the presence of the *n*-conductor zinc oxide [19, 20, 36], cadmium oxide [22], and the insulator magnesium oxide [7, 24] is contradictory to the above assumption. The activation energies of the catalytic reactions agreed again with the value ascribed to the electron-transfer process.

Detailed investigations showed, however, that the role of the oxides in these cases fundamentally differed from those above. It was an essential difference that all three oxides reacted with the AP according to the following reaction:



The fact that the perchlorate salts formed exerted similar effects on the above oxides permitted the conclusion that not the oxides but the perchlorate salts formed in the above reaction were responsible for the observed acceleration of the reaction [20, 22, 24]. This is supported by the finding that, when a small amount of additive is used, the rate of decomposition is the same in the presence of the perchlorate or of the oxide; the time lag, however, is longer in the presence of the oxide. This difference is clearly caused by the fact that, in the case of the oxides, the formation of the catalyst must precede the catalytic reaction, *i.e.* the oxide must react with the AP. As regards the decomposition of AP, this reaction is primarily disadvantageous; the reaction between the two substances presumably occurs with the participation of the most active surface centres which are also of primary importance for the decomposition. (The decomposition of AP begins on the surface.) On using small amounts of oxide this effect appears either not at all or only to a small extent; in the presence of a larger amount, however, at higher temperature it can assume such an extent that the decomposition of AP commences later than in the absence of the oxide. The interpretation of the effects of metal perchlorates is dealt with below.

From the kinetic data given in the previous paper [1] it is clear that, in many cases, the raising of the temperature region is accompanied by the increase of the activation energy of the catalytic reaction. Disregarding a few abnormal values, it is found that the values of the higher activation energy fall in the range 40–45 kcal.

This increase of the activation energy can be interpreted as due to the change in the mechanism of the catalytic decomposition and of the rate-determining step. It was assumed earlier that in this case the primary reaction is the decomposition of the perchlorate ion, where the slowest process is the rupture of the Cl-O bond. Since the dissociation energy of this bond (63.3 kcal) is substantially higher than the activation energy values obtained from kinetic measurements, HERMONI and SALMON [7] assumed that both the electron-transfer process (32 kcal) and the decomposition of the perchlorate ion (63 kcal) play a part in the decomposition of AP. The 40–45 kcal is derived from the above two values. However, it cannot be excluded that, in the presence of oxides, the decomposition of the perchlorate ion proceeds with a smaller activation energy. This is supported by experiments with alkali chlorates and perchlorates. The activation energies of the uncatalysed reaction well approximate the value of the dissociation energy of the Cl-O bond [40–43]. In the presence of the effective transition metal oxides, however, the value of the activation energy was significantly smaller [40, 44].

After the development of these mechanisms for the catalytic decomposition of AP, more recent kinetic and other investigations with pure AP brought about a fundamental change [45]. This work is summarized as follows.

(a) Repeated kinetic measurements on both the low and the high temperature decomposition and the sublimation of AP led to identical activation energies of 30 kcal.

(b) Mass-spectrographic studies did not confirm the existence of the molecular complex and definitely showed that the primary step in the decomposition of AP is the dissociation to ammonia and perchloric acid.

(c) Calculations, using the most reliable physical data, of the thermal activation energy value necessary for the electron-transfer in AP gave substantially larger values than the above (33—35 kcal).

From all this it was assumed that, regardless of the temperature range, AP decomposes by a proton-transfer process. Although a number of authors consider the generalized proton-transfer model [46] as over-simplified and maintain the view that the decomposition mechanism of AP varies with the temperature region [47, 48], it is certain that many facts reported in detail in the previous paper [49] prove the general importance of the proton-transfer process.

On the basis of the proton-transfer model, the interpretation given by JACOBS and RUSSEL-JONES [12] for the decomposition of AP catalysed by copper chromite was that the perchloric acid formed during the dissociation of the AP migrates to the surface of the oxide and there decomposes in a heterogeneous phase reaction. The following steps comprise the oxidation of ammonia by the decomposition products of the perchloric acid. A proof of this route for the catalysis is provided by the fact that the oxides also exhibited catalytic effects when they were physically separated from the AP [2, 3]. Another result which may be regarded as important in this respect was that the effect of nickel oxide mixed with AP, regardless of the quantity, depended on the extent of the BET surface [3].

Since the activation energy of the catalysed decomposition (45 kcal) agreed with the activation energy of the homogeneous phase decomposition of perchloric acid, the authors assumed that the rate-determining process was the decomposition of perchloric acid on the surface of the oxide.

This latter conclusion is, however, subject to criticism, since it is difficult to imagine that the catalysed and non-catalysed decompositions should take place with the same activation energy values [14, 15, 50]. Study of the decomposition of HClO_4 catalysed by chromic oxide confirms this doubt [15].

Since the dissociative vaporization of AP becomes more important at higher temperature (300°C), this reaction path seems very plausible at least at higher temperatures, and with high probability, such an effect on the high-temperature decomposition of AP is exerted by the other oxides, too.

It is questionable, however, whether at low temperature (below 240 or 200°C), where the dissociative vaporization of AP is extremely small, the catalytic decomposition of AP proceeds in this way. The fact that the activity series of the oxides differ somewhat in the low and the high temperature region may be an indication of different reaction mechanisms.

From a consideration of the products of the catalysed and non-catalysed reactions and of the oxidation of the $\text{CuO}\cdot\text{Cr}_2\text{O}_3$ catalyst, WISE [8] came to the

conclusion that in contrast with the decomposition of pure AP the catalysed reaction proceeds according to the electron-transfer mechanism given above.

Knowledge of the catalytic decomposition of perchloric acid appeared fundamentally important for the elucidation of the mechanism of the catalytic decomposition of AP, since the literature did not contain any data in this respect. The main results of investigations carried out recently in this field by the author of this paper and his colleagues are given in Table V [4, 14, 15, 51].

Table V
Kinetic data of the catalytic decomposition of perchloric acid [49]

Catalyst	Temperature range of the reaction, °C	k_{spec} ($\text{sec}^{-1} \text{m}^{-2}$) at 300°C	Activation energy, kcal/mole	% conversion at 300°C m^{-2}
Cr ₂ O ₃	150—180	—	31.0	39.8*
MnO	210—250	3.9585	27.1	9.7**
CuO	270—300	1.4350	42.8	38.3
CO ₂ O ₃ —CO ₂ O ₄	210—260	(1.4)	—	20.5
Fe ₂ O ₃	250—285	0.5831	42.6	20.2
Al ₂ O ₃	240—290	0.2942	26.5	10.6
SnO ₂	295—340	0.2220	20.7	5.8
TiO ₂	305—330	0.0350	33.0	0.86
ZnO	330—335	0.0154	45.6	0.40
CdO	400	—	—	—
MgO	400	—	—	N.D.***
SiO ₂	400	—	—	N.D.***
CaO	400	—	—	N.D.***

* At 180°C ** At 250°C *** No decomposition

To characterize the effectiveness of the oxides, the temperature ranges of the decomposition were given together with the first order rate constants measured at or extrapolated to 300°C. On this basis, the catalysts were divided into three groups.

(a) Particularly effective oxides which display considerable catalytic action even at 130°C (chromic oxide) or 240—290°C (cobalt, nickel, copper, iron and aluminium oxides).

(b) Less effective oxides (tin dioxide, titanium dioxide, zinc oxide) which catalyse the decomposition of perchloric acid at 300—360°C.

(c) Inactive oxides (cadmium, magnesium and calcium oxides) in the presence of which catalytic reaction was not observed.

The apparent activation energies of the catalytic reaction fall in the range 20—45 kcal.

From a comparison of the data of Tables I and V it is quite clear that the activity series for the oxides are significantly different in the two decomposition reactions. Chromic oxide, which proved the most effective substance as regards the decomposition of perchloric acid, affected the slow decomposition of AP only to a small extent. Aluminium oxide, titanium dioxide and tin dioxide, which exerted only a very slight effect on the decomposition and explosion of AP, catalysed the decomposition of perchloric acid fairly well. Nickel, cobalt and copper oxides are

effective catalysts of the slow decomposition of AP [7, 27], but catalyse the decomposition of perchloric acid at a considerably higher temperature than does the less active chromic oxide.

On the basis of all these facts, the mechanism proposed by JACOBS for the catalysed reaction seems to be an over-simplification, or at least cannot be generally applied. The experiment referred to in JACOBS' review [45] that NH_3 streaming over the potassium perchlorate catalyst system did not ignite even above the ignition temperature of AP cannot be considered as a proof of his theory. This was interpreted by JACOBS to mean that the catalysts act on the HClO_4 and not on the ClO_4^- anion. The oxides effective in the decomposition of AP are also very good catalysts in the decompositions of potassium perchlorate and other alkali metal perchlorates. There are many possible reasons for the failure to ignite: a different decomposition mechanism; the substantially higher stability than that of AP (the pure salt decomposes above 560°C); etc.

The fact that the series of effectiveness of the oxides in the low temperature decomposition of AP essentially agrees with the series found in the oxidation of ammonia permits the conclusion that the oxidation of ammonia plays a substantially greater part in the catalytic process than was assumed. Since the electrical properties of the catalysts are decisive in the oxidation of ammonia with molecular oxygen, and the rate of oxidation increases with increasing p -character of the catalyst, it cannot be excluded that the essential role of the electrical properties of the oxides is to be ascribed to their role in oxidizing ammonia in the decomposition of AP.

It is highly probable that the effectiveness of the oxides is due to two factors: the catalysis of the heterogeneous phase decomposition of perchloric acid, and the catalysis of the oxidation of ammonia. Oxides able to catalyse both reactions can be considered as most effective. This also means that the decisive step in each reaction occurs on the surface of the catalyst, presumably in such a way that the adsorbed ammonia is oxidized by the radicals formed in the decomposition of the adsorbed perchloric acid (O , ClO , ClO_2). If the temperature and reaction conditions are altered, then, depending on the properties of the oxide, the adsorption of HClO_4 and NH_3 , and the decomposition of adsorbed HClO_4 change, and this may lead to the modification of the series of effectiveness of the oxides with the temperature region.

It is not possible to decide on the basis of the data available at present whether the direct reaction between the ammonia and the perchloric acid does proceed on the surfaces of the oxides. According to unpublished measurements, the above reaction occurs in the homogeneous phase [45].

The fact that the gas phase decomposition of AP ($\text{NH}_3 + \text{HClO}_4$) on ZnO proceeds with a well-measurable rate at temperatures where neither the ZnO-catalysed decomposition of HClO_4 nor the oxidation of NH_3 takes place, permits conclusions on the promotion of the direct reaction between the two substances [5, 51]. The optimum adsorption of the substances appears necessary for the catalysis of the reaction; according to the above, this is available on ZnO in spite of the fact that ZnO is not an outstanding catalyst for either the decomposition of HClO_4 nor the oxidation of NH_3 .

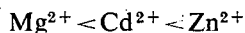
2. Mechanism of action of salts

A further question remains concerning the interpretation of the accelerating action of various salts, primarily of metal ions introduced in the form of perchlorates.

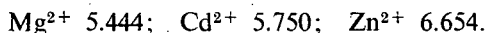
In the first works the effects of the ions were similarly explained on the basis of the electron-transfer mechanism. Silver, copper and iron perchlorates proved to be particularly effective substances [52, 53]. Since these metal ions are effective electron acceptors, it was assumed that, like the *p*-type oxides, they promote the formation of the perchlorate radical, and increase its lifetime and the probability of its decomposition [52, 53]. The effects of bromide and iodide ions were also explained by the electron-transfer reaction [52]. The role of chlorate ions in decreasing the stability of AP to a large extent was likewise explained by the electron-transfer mechanism, the chlorate radical formed acting both as an electron acceptor and also as a radical producer, promoting thereby the reaction [54—56].

However, it cannot be expected that the zinc, cadmium and magnesium ions participate directly in the electron-transfer reaction between the ammonium and perchlorate ions, accelerating by this means the electron-transfer. It appears much more probable that the increased tendency to decompose of the AP is the result of its partial melting [19, 20, 22, 24, 57, 58], though the melting point of pure AP is not known since the substance explodes before the melting point is reached. However, in the presence of the perchlorate salts in question (and also of the corresponding oxides) AP was observed to melt at the temperature of the experiments. This can be conceived in the present case as due to the formation of an eutectic of lower melting point between the AP and the perchlorate added.

In addition, the polarizing effects of the metal ions should also play a part in the action of the additives; the greater the polarizing power (effective electric field strength) of the cations, the greater their accelerating action on the reaction [22, 57, 58]. The series of effectiveness of the substances:



corresponds to the series of effective electric field strengths of the cations:

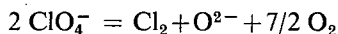


It should be remembered that the effective electric field strengths of the cations play an important part in determining the thermal stabilities of metal perchlorates: the higher the value, the lower the stability of the substance [41—43, 59]. The significance of the polarizing power of the cations is shown by the fact that, although lithium perchlorate causes the melting of AP, it does not exhibit the large acceleration of the reaction observed for magnesium, cadmium and zinc ions [60]. Similarly, the other alkali metal perchlorates and calcium perchlorate did not possess a catalysing action. It is well known that the polarizing power of the alkali metal ions is the lowest, their effective electric field strengths increasing from caesium to lithium from 1.3 to 2.9. At all events, however, the melting of the mixtures seems necessary for the polarizing action of the cations to be exerted. This can be seen from the fact that, when magnesium, cadmium and zinc ions were added in the form of their sulphates to the AP, no acceleration occurred and the AP did not explode even at 400°C [22, 57, 58]. The melting points of magnesium, cadmium and zinc sulphates are extremely high, and their mixtures with AP did not melt, even partially below 400°C.

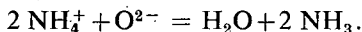
It was, however, an open question up to now, by what mechanism AP decomposes in the presence of the above metal ions and how these ions are involved in this mechanism. Leaving out of consideration the above findings, RUSSEL—JONE and JACOBS [61] explained the actions of these metal ions and of silver by ammin formation and hence the promotion of the proton-transfer process. This explanation is, however, not very probable because almost the same effects were exerted by $\text{Zn}(\text{NH}_3)_2(\text{ClO}_4)_2$ and $\text{Zn}(\text{ClO}_4)_2$ [57]. In addition, at the temperature of the decomposition of AP the reaction



proceeds almost completely towards the left, and thus, at this temperature, the above process can be excluded. The situation is completely similar in the case of the cadmium salt, too [62]. Irrespective of this fact, it would be difficult to imagine that the tremendous acceleration effect of a very small amount of the perchlorate salt ($\text{AP}:\text{Zn}(\text{ClO}_4)_2$, molar ratio 1000:1) would result merely from the displacement of the dissociation of the AP. In the view of JACOBS and ACHESON [63], in the presence of magnesium perchlorate, oxide ions are formed from the decomposition of the perchlorate ion in the molten phase



and these, as effective proton acceptors, promote the formation of ammonia

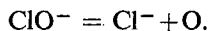
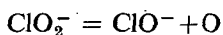
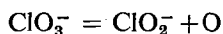
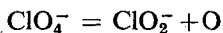


In our opinion, this reaction path is not probable either, since in the decomposition of zinc perchlorate, which is more effective than magnesium perchlorate, predominantly chloride ions are formed, and the decomposition of the likewise effective cadmium perchlorate does not lead to the formation of oxide ions at all.

We consider that in interpreting the actions of perchlorate salts it is essential to rely on the findings reported above, according to which the partial melting of the mixture and the high polarizing power of the cations are necessary for the emergence of the accelerating effect. In studying the thermal decomposition of various perchlorate salts it was observed [41—43] that the melting of the mixtures is accompanied by the substantial increase by (1—2 orders of magnitude) of the rate of decomposition. This is probably caused by the increased mobility of the ions and the ceasing of the restriction of the reaction to the surface (external and internal) of the crystals. In the present case the following ions can be considered in the molten phase: M^{2+} , ClO_4^- and NH_4^+ . If the latter dissociates partially, then H^+ and NH_3 are also formed.

The decomposition of the perchlorate ion in the melt begins depending on the polarizing power of the metal ion. This means that in the presence of the metal ions, in a molten phase a new reaction path is available for the decomposition of the perchlorate ion, a path which played essentially no role in the absence of the metal ions, in other words in solid AP. Earlier investigations showed clearly that

the perchlorate salts of both alkali metals and bivalent metals decompose stepwise with the transitional formation of chlorate and chlorite:



The disproportionation of the oxy anions of chlorine takes place parallel to the decomposition. The slowest step in the decomposition of perchlorates is the first reaction. If only the first step is considered, it is evident that both the chlorate ion, which is extremely effective as regards the decomposition of AP, and the oxygen atom necessary for the oxidation of ammonia are formed. Both products can bring about the increase of the rate of decomposition.

Considering the presence of NH_4^+ and NH_3 , it is very unlikely that the decomposition of the chlorate ion proceeds in the above way. Ammonium chlorate is an extremely unstable substance, slowly decomposing even at 40–50 °C, and exploding above 70°C [64]. Its decomposition is assumed to occur in a proton-transfer process; the unstable HClO_3 formed decomposing, the radicals proceed oxidizing the ammonia.

Accordingly the most probable reaction path seems to be the formation of HClO_3 by reaction of ClO_3^- ions with free H^+ or with protons from NH_4^+ ; the HClO_3 rapidly decomposing with the formation of the radicals necessary for the oxidation of ammonia.

This reaction path is in agreement with experimental observations. The decomposition of the perchlorate ion in the molten phase occurs only in the presence of cations of high polarizing power. When lithium perchlorate was used, although the mixture melted, the extremely powerful catalytic effect observed in the presence of zinc, cadmium and magnesium ions did not occur, since the polarizing power of the lithium ion is substantially lower than that of these other metal ions [60]. For similar reasons, no acceleration of the reaction occurred with barium [65] and calcium perchlorates [62], although both substances caused partial melting of the AP. In the case of zinc, cadmium and magnesium sulphates, no catalytic effect was observed, because the mixture remained in the solid phase [22, 58].

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МЕХАНИЗМ КАТАЛИТИЧЕСКОГО РАЗЛОЖЕНИЯ ПЕРХЛОРАТА АММОНИЯ

Ф. Шоймоши

В работе дан критический обзор разных взглядов, связанных с влиянием различных добавок на термическое разложение и горение перхлората аммония. На основании всех данных и наблюдений нами предлагается механизм каталитического разложения перхлората аммония.