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FEATURES OF THE INITIAL STAGES OF LOW-
TEMPERATURE DECOMPOSITION OF AMMONIUM
PERCHLORATE

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Foreign Technology Division
Wright-Patterson Air Force Base, Ohio

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	<i>А а</i>	A, a	Р р	<i>Р р</i>	R, r
Б б	<i>Б б</i>	B, b	С с	<i>С с</i>	S, s
В в	<i>В в</i>	V, v	Т т	<i>Т т</i>	T, t
Г г	<i>Г г</i>	G, g	У у	<i>У у</i>	U, u
Д д	<i>Д д</i>	D, d	Ф ф	<i>Ф ф</i>	F, f
Е е	<i>Е е</i>	Ye, ye; E, e*	Х х	<i>Х х</i>	Kh, kh
Ж ж	<i>Ж ж</i>	Zh, zh	Ц ц	<i>Ц ц</i>	Ts, ts
З з	<i>З з</i>	Z, z	Ч ч	<i>Ч ч</i>	Ch, ch
И и	<i>И и</i>	I, i	Ш ш	<i>Ш ш</i>	Sh, sh
Й й	<i>Й й</i>	Y, y	Щ щ	<i>Щ щ</i>	Shch, shch
К к	<i>К к</i>	K, k	Ъ ъ	<i>Ъ ъ</i>	"
Л л	<i>Л л</i>	L, l	Ы ы	<i>Ы ы</i>	Y, y
М м	<i>М м</i>	M, m	Ь ь	<i>Ь ь</i>	'
Н н	<i>Н н</i>	N, n	Э э	<i>Э э</i>	E, e
О о	<i>О о</i>	O, o	Ю ю	<i>Ю ю</i>	Yu, yu
П п	<i>П п</i>	P, p	Я я	<i>Я я</i>	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
 When written as ё in Russian, transliterate as yë or ë.
 The use of diacritical marks is preferred, but such marks
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RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}
rot	curl
lg	log

GREEK ALPHABET

Alpha	A	α	α	Nu	N	ν
Beta	B	β		Xi	Ξ	ξ
Gamma	Γ	γ		Omicron	Ο	ο
Delta	Δ	δ		Pi	Π	π
Epsilon	E	ε	ε	Rho	Ρ	ρ ϑ
Zeta	Z	ζ		Sigma	Σ	σ ς
Eta	H	η		Tau	Τ	τ
Theta	Θ	θ	θ	Upsilon	Υ	υ
Iota	I	ι		Phi	Φ	φ ϕ
Kappa	K	κ	κ	Chi	Χ	χ
Lambda	Λ	λ		Psi	Ψ	ψ
Mu	Μ	μ		Omega	Ω	ω

FEATURES OF THE INITIAL STAGES OF LOW-TEMPERATURE DECOMPOSITION OF AMMONIUM PERCHLORATE

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In the majority of works the kinetics of the decomposition of ammonium perchlorate (APC) [ПХА] was studied with respect to the pressure and composition of the gaseous products of thermal decomposition or with respect to the weight loss in the heating process. The findings made it possible to determine the features of the kinetics and the many sides of the mechanism of the very complex process of APC decomposition [1-4]. At the same time, for rigorous substantiation of the APC decomposition mechanism supplementary research on the kinetics of decay product accumulation in the condensed phase is necessary.

Hence, in the initial stages of APC decomposition in the temperature range 160-220°C we studied the composition of the chlorine-containing thermolysis products and also weight losses. Thermolysis was realized at atmospheric pressure under conditions of the equilibrium of the decomposing APC with the decay products in the gaseous phase. By the method of potentiometric titration and spectrophotometry in the ultraviolet range we determined the

contents of the chlorine, chloride-ions, sum of oxychloro-anions and perchloric acid. In the operation we used a technical APC with average particle size $\sim 100 \mu$.

As a result of the investigations it was shown that in the early stages of decomposition in the condensed phase an analytically determined quantity of chlorine oxides are absent, while the basic thermolysis products are Cl_2 , HCl , and HClO_4 .

The comparison of data on the kinetics of the accumulation of thermolysis products in the condensed phase with the kinetics of weight loss (in a recalculation of the appropriate number of ClO_4^- ions) shows that even with the degree of decomposition (η)=0.1-0.15 the percentage of decay products in the condensed phase is $\sim 20\%$ [5], but in the early stages it is still more (Figs. 1 and 2).

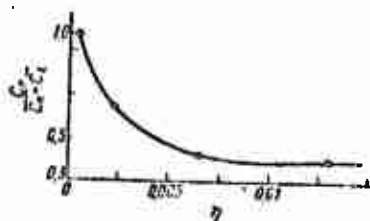
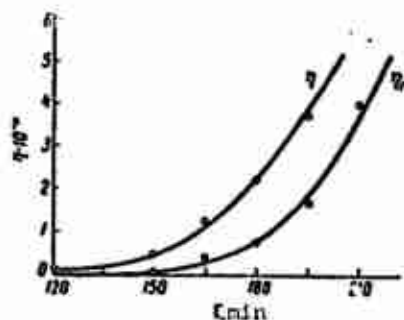


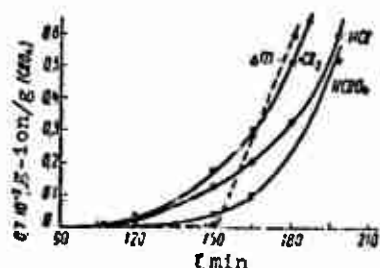
Figure 1. Dependence of the ratio of the concentration of thermolysis products of ammonium perchlorate in the condensed phase to the total quantity of the decomposing substance ($\frac{C_k}{C_t}$) on the total percentage of decomposition at $+190^\circ\text{C}$.

Figure 2. Dependence of the percentage of decomposing ammonium perchlorate on time at $+190^\circ\text{C}$. η_m - weight loss; η - total percentage of decomposition taking into account products in the condensed phase.



At the beginning of the induction period (at 190°C for 100 min) the process continues so slowly that the thermolysis products cannot be detected, but then a rapid increase occurs in the concentration of Cl_2 , HCl , and HClO_4 in the condensed phase; the induction period with respect to weight loss is one and a half times more (Fig. 3). It is especially important that perchloric acid in the induction period not accumulate in analytically determined quantities and its formation occur simultaneously with the remaining thermolysis products. The maximum concentration of perchloric acid in the condensed phase reaches 0.1-0.2% (in relation to the initial APC) and is realized at the stage of maximum acceleration of the thermolysis process ($\eta=0.07-0.1$); subsequently, (to $\eta=0.15$) its contents are unchanged, and then smoothly fall.

Figure 3. Dependence of the concentration of thermolysis products of ammonium perchlorate on time at +190°C in the condensed phase and weight loss of (Δm) in a recalculation of the appropriate quantity of ClO_4^- g-ion/g.



The analysis of the ratio of the formation rates of $\text{Cl}_2 + \text{HCl}$ (w_1) and HClO_4 (w_2) shows that in the initial stages (in the induction period with respect to weight loss approximately 150 min at 190°C) $w_1/w_2 \approx \text{const}$ (Fig. 4).

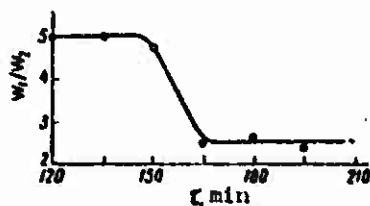
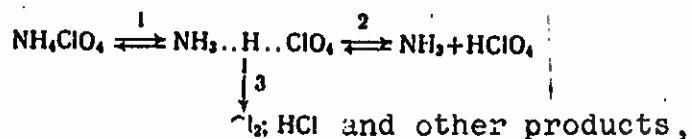


Figure 4. Dependence of the ratio of the formation rates of ($\text{Cl}_2 + \text{HCl}$) and (HClO_4) in the condensed phase on time.

From this it follows that Cl_2 and HCl are not the decay products of perchloric acid, but are formed from APC independently.

It is known that low-temperature decomposition continues at a greater rate than sublimation under corresponding conditions [4].

The given experimental results together with this fact are not layed out in the framework of the APC decomposition diagram proposed by Jacobs and Russel-Jones [6]. Hence, it is assumed that at least in the early stages of decomposition APC thermolysis products can be formed by the following diagram:



i.e., the limiting APC thermolysis stage is reaction 1, not 2. This diagram agrees with the obtained results and with most of the data on the effect of different factors on low temperature APC thermolysis.

The obtained results indicate the significant role of the processes in the condensed phase during APC thermolysis. The thermolysis products in the condensed phase must be considered in the early stages of decomposition.

The dissociation reaction in NH_3 and HClO_4 and subsequent reactions with the participation of these products in the early stages of low-temperature thermolysis of ammonium perchlorate are not limiting processes.

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