

INVESTIGATION OF THE COMBUSTION OF ORGANIC PERCHLORATES

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A comparison of the combustion rates of various nitro compounds [1] shows that they burn with close and relatively low rates. This is probably connected with the fact that, in the combustion of such substances, most of the heat is evolved by the oxidation of the organic (combustible) part of the molecule of exactly the same oxidizer, i.e., oxygen-containing nitrogen compounds having a relatively low reactivity, for example, perchloric acid and chlorine acids. Therefore, it is to be expected that replacement of the NO_2 group in the molecule of an explosive compounds by a more active oxidizer, for example Cl^{7+} , will lead to a substantial increase in the combustion rate. Actually, gas mixtures in which the oxidizers are oxygen-containing compounds burn not only more rapidly than mixtures with nitrogen oxides, but also than mixtures with oxygen [2-5]. A preliminary study of organic perchlorates [6, 7] has shown that they burn 7-10 times faster than secondary explosives. In addition, for some perchlorates completely unexpected dependences $u(p)$ were obtained. In view of this, it seemed of interest to make a systematic study of the combustion of compounds of this class.

Experimental Method

The tests were made in a constant-pressure bomb (1-400 atm). The character and rate of the combustion were recorded photographically. The perchlorates were obtained by reaction between amines or their chloride, nitrate, acetate or carbonate salts and 57% perchloric acid. When the reaction was carried out using amine salts, the forming HCl , HNO_3 , and CH_3COOH were removed in a boiling-water bath. Perchlorates of polyamines were recrystallized from perchloric acid, and perchlorates of monoamines from water or alcohol; polyamine monoperchlorates were recrystallized twice from water and once from alcohol. All the salts were repeatedly washed with ether and dried in vacuum at a temperature of 20-100° C to constant weight. The charges were pressed into Plexiglas tubes of diameters 4 or 7 mm under a pressure of 1000-5000 atm. The substances and the charges were stored in a desiccator over P_2O_5 .

Experimental Results

Perchlorates of Aliphatic Amines. The dependences $u(p)$ for the perchlorates of aliphatic amines are given in Figs. 1-3 and Table 1. All these compounds can be regarded as ammonium perchlorates in which the hydrogen atoms have been replaced by various hydrocarbon radicals. The introduction of a methyl radical into a molecule of ammonium perchlorate leads to a very sharp increase in the combustion rate (by almost one order of magnitude). However, methylamine perchlorate, like ammonium perchlorate, has a discontinuity on the curve for $u(p)$. In the interval 11-60 atm, the charge cannot be ignited. With ignition, there is a spark, as a result of which the charge burns down by a distance of 0.5-1 mm and then dies out. It was found impossible to measure the combustion rate of methylamine perchlorate at high pressures, since, starting at 230 atm, the combustion becomes unstable; after a small sector of equilibrium combustion, the flame jumps into the depths of the charge; under these circumstances, the casing is pulverized into small fragments.

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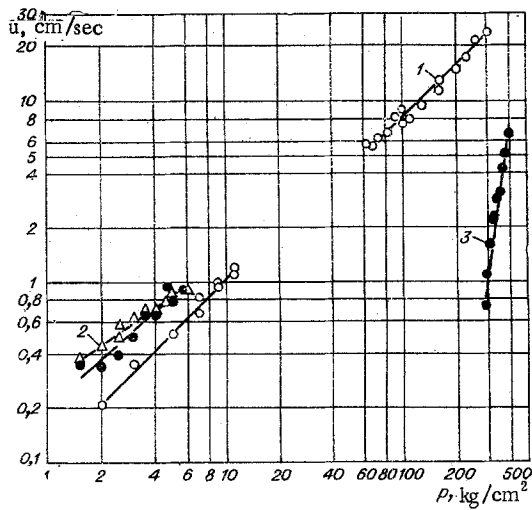


Fig. 1

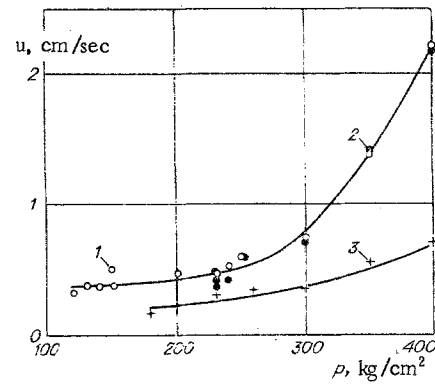


Fig. 2

Fig. 1. Dependences $u(p)$ for methylamine (1), dimethylamine perchlorate (2), and trimethylamine perchlorate (3).

Fig. 2. Dependences $u(p)$ of butylamine perchlorates: 1) n-butylamine perchlorate; 2) iso-butylamine perchlorate; 3) secondary butylamine perchlorate.

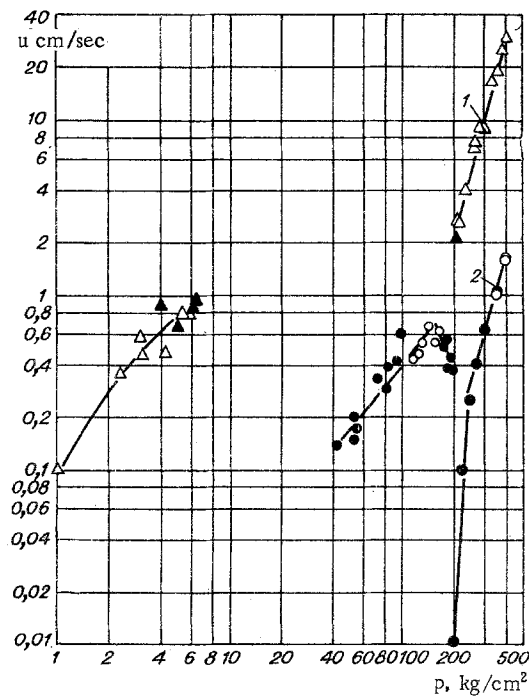


Fig. 3. Dependences $u(p)$ for ethylamine perchlorate (1) and diethylamine perchlorate (2). The solid points represents combustion under pulsed conditions.

TABLE 1

Substance	Pressure range, atm	Dependence of combustion rate (cm/sec) on pressure (atm)
Methylamine perchlorate $\text{CH}_3\text{NH}_2 \cdot \text{HClO}_4$	2-10 11-60 60-300	$u=0,107 p$ Does not burn $u=0,4+7,8 \cdot 10^{-3} p$
Dimethylamine perchlorate $(\text{CH}_3)_2\text{NH} \cdot \text{HClO}_4$	1,5-6 7-100 100	$u=0,28 p^{0,68}$ Does not burn Explodes
Trimethylamine perchlorate $(\text{CH}_3)_3\text{N} \cdot \text{HClO}_4$	1,5-6 7-290 290-400	$u=0,15 p^{0,83}$ Does not burn $u=2,7 \cdot 10^{-17} p^{6,68}$
Tetramethylamine perchlorate $(\text{CH}_3)_4\text{N}^+ \text{ClO}_4^-$	1-400	Does not burn
n-Butylamine perchlorate $\text{CH}_3(\text{CH}_2)_3\text{NH}_2 \cdot \text{HClO}_4$	120-230 230-400	$u=8 \cdot 10^{-3} p^{0,035}$ $u=3,5 \cdot 10^{-7} p^{2,6}$
Isobutylamine perchlorate $(\text{CH}_3)_2\text{CHCH}_2\text{NH}_2 \cdot \text{HClO}_4$	230-400	$u=3,5 \cdot 10^{-7} p^{2,6}$
Secondary butylamine perchlorate $\text{CH}_3\text{CH}_2\text{CHNH}_2 \cdot \text{HClO}_4$	180-400	$u=2,9 \cdot 10^{-3} p^{1,7}$
Ethylamine perchlorate $\text{CH}_3\text{CH}_2\text{NH}_2 \cdot \text{HClO}_4$	1-7 8-200 200-400	$u=-0,15+2,5 \cdot 10^{-1} p^{0,77}$ Does not burn $u=5 \cdot 10^{-9} p^{3,76}$
Diethylamine perchlorate $(\text{CH}_3\text{CH}_2)_2\text{NH} \cdot \text{HClO}_4$	41-150 150-193 194-199 200-240 240-400	$u=1,6 \cdot 10^{-3} p^{1,2}$ $u=2,7 \cdot 10^3 p^{-2,55}$ Does not burn Rate increases by 25 times $u=1,3 \cdot 10^{-9} p^{3,5}$

The introduction of secondary and tertiary methyl radicals into a molecule of ammonium perchlorate leads, on the other hand, to a further, actually insignificant, increase in the combustion rate at low pressures and, on the other hand, to a broadening of the pressure range in which the combustion is not propagated.

A perchlorate containing four methyl radicals in its molecule could not be ignited at any of the pressures investigated (1-400 atm). The lack of combustion is not connected with the fact that a molecule of perchlorate is overcharged with combustible, since the isomers of tetramethyl ammonium perchlorate, butylamine perchlorates, and diethylamine perchlorate were found to be capable of combustion under these conditions. Butylamine perchlorates (Fig. 2) start to burn at high pressures (120-230 atm). At low pressures and with a vacuum (down to 0.01 atm) the charges could not be ignited. With ignition in a vacuum, the substance is first melted, and then the melted layer starts to bubble and is thrown out of the tube. If the pressure was close to atmospheric, the molten layer flared up and ignited rapidly, but the combustion was not propagated further.

Diethylamine perchlorate burns considerably slower than ethylamine perchlorate and has a unique $u(p)$ dependence. Combustion starts only at 41 atm. At the start, the rate rises, and then falls. In a very narrow range, 194-199 atm, the charge cannot be ignited. At 200 atm, combustion is renewed ($u = 0.01$ cm/sec) but takes place at a very irregular rate: sometimes it stops in the forward movement of the front attain several seconds. The pulsation disappears only at 350-400 atm. After renewal of the combustion, the rate rises rapidly with pressure (with a change in the pressure from 200 to 240 atm, it increases by 25 times). After 240 atm, the rate of rise is slowed down somewhat.

We turn now to the perchlorates of aliphatic polyamines. The dependences $u(p)$ for these compounds are given in Figs. 4 and 5, and in Table 2. Diethylenetriamine triperchlorate and ethylenediamine diperchlorate (Fig. 4), in distinction from the perchlorates considered above, burn over the whole pressure range investigated. An increase in the length of the hydrocarbon chain between the amine groups in a molecule of diperchlorate radically changes the form of the dependence $u(p)$. In distinction from ethylenediamine diperchlorate, tetramethyldiamine diperchlorate and hexamethyldiamine diperchlorate have "discontinuities" on the $u(p)$ curve. We note that, before extinction, combustion takes place under pulsed conditions and that its rate decreases sharply. At the same time, the luminescence brightness also decreases. For tetramethylenediamine diperchlorate in the region of 37 atm, the rate varies from 4.2 to 1-1.3 cm/sec; it varies so sharply that it was not possible to obtain intermediate values. If the charge is ignited at 36 atm, and the pressure in the bomb is lowered as a result of the gases forming

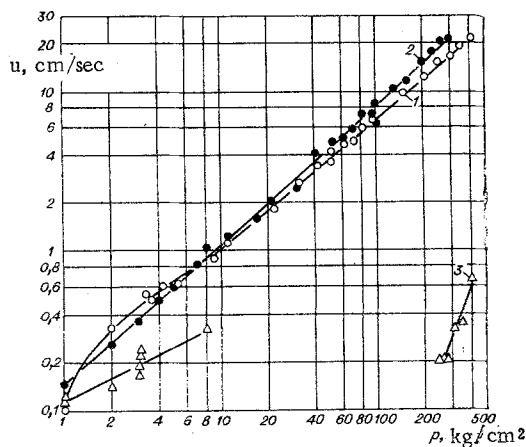


Fig. 4

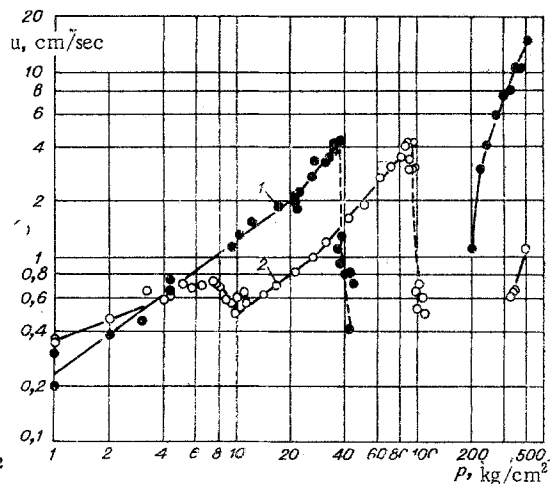


Fig. 5

Fig. 4. Dependences $u(p)$ of ethylenediamine diperchlorate (1), diethylenediamine triperchlorate (2), and ethylenediamine monoperchlorate (3).

Fig. 5. Dependences $u(p)$ of tetramethylenediamine diperchlorate (1) and hexamethylenediamine diperchlorate (2).

TABLE 2

Substance	Pressure range, atm	Dependence of combustion rate (cm/sec) on pressure (atm)
Ethyldiamine diperchlorate $O_4ClH \cdot H_2N(CH_2)_2NH_2 \cdot HClO_4$	1-20	$u = -0,13 + 2,3 \cdot 10^{-1} p^{0,68}$
	20-400	$u = 0,14 p^{0,85}$
Ethyldiamine monoperchlorate $H_2N(CH_2)_2NH_2 \cdot HClO_4$	1-8	$u = 0,12 p^{0,3}$
	9-250	Does not burn
	250-400	$u = 2,4 \cdot 10^{-7} p^{2,46}$
Diethylenetriamine triperchlorate $O_4ClH \cdot HN \begin{cases} CH_2CH_2NH_2 \cdot HClO_4 \\ CH_2CH_2NH_2 \cdot HClO_4 \end{cases}$	1-300	$u = 0,15 p^{0,89}$
Tetramethylenediamine diperchlorate $O_4ClH \cdot H_2N(CH_2)_4NH_2 \cdot HClO_4$	1-21	$u = 0,24 p^{0,7}$
	21-37	$u = 7 \cdot 10^{-2} p^{1,14}$
	37-48	Sharp drop in rate
	48-200	Does not burn
	200-400	$u = -11,5 + 6,35 \cdot 10^{-2} p$
Hexamethylenediamine diperchlorate $O_4ClH \cdot H_2N(CH_2)_6NH_2 \cdot HClO_4$	1-7	$u = 0,36 p^{0,38}$
	7-10	$u = 15 p^{-1,46}$
	10-26	$u = 0,1 p^{0,7}$
	26-92	$u = 2,5 \cdot 10^{-2} p^{0,7}$
	92-110	Sharp drop in rate
	110-330	Does not burn
	330-400	$u = -2 + 7,9 \cdot 10^{-3} p$

above 37 atm, a jumpwise change in the rate is clearly visible from the photoscanning. It is of interest that tetramethylenediamine diperchlorate, up to 37 atm, burns approximately 30% faster than ethylenediamine diperchlorate. With the combustion of hexamethylenediamine diperchlorate, in distinction from ethylenediamine and tetramethylenediamine perchlorates, a considerable amount of soot is formed during the combustion process.

Ethylenediamine monoperchlorate, like the perchlorates of aliphatic monoamines, has a pressure interval in which the combustion is not propagated.

Perchlorates of Aromatic Amines. The dependence $u(p)$ for simplest of the aromatic perchlorates is shown in Fig. 6. Aniline perchlorate burns over the whole pressure range investigated; however, with a rise in the pressure, the course of the curve $u(p)$ varies by several times (Table 3). The introduction of nitro groups into aniline perchlorate leads to a small increase of the combustion rate only in the interval 2-200 atm (Fig. 6, Table 3). Above 200 atm, both compounds burn at an identical rate.

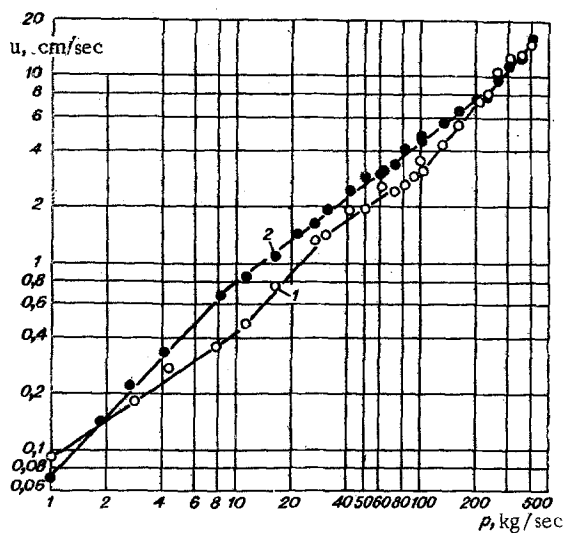


Fig. 6. Dependences $u(p)$ for aniline perchlorate (1) and *m*-nitroaniline perchlorate (2).

TABLE 3



Aniline perchlorate $\text{NH}_2 \cdot \text{HClO}_4$ 		<i>m</i> -Nitroaniline perchlorate $\text{NH}_2 \cdot \text{HClO}_4$ 	
pressure range, atm	dependence of combustion rate (cm/sec) on pressure (atm)	pressure range, atm	dependence of combustion rate (cm/sec) on pressure (atm)
1-10	$u = 9 \cdot 10^{-2} p^{0.69}$	1-8	$u = 7 \cdot 10^{-2} p^{1.07}$
10-30	$u = 3,5 \cdot 10^{-2} p^{1.1}$	8-200	$u = 1,4 \cdot 10^{-1} p^{0.75}$
30-100	$u = 1,5 \cdot 10^{-1} p^{0.67}$	200-400	$u = 1,7 \cdot 10^{-2} p^{1.14}$
100-400	$u = 1,7 \cdot 10^{-2} p^{1.14}$		

Figure 7 gives the dependences $u(p)$ for isomers of the composition $\text{C}_7\text{H}_{10}\text{NClO}_4$. A characteristic of all the compounds is the presence of a region of additives in which the combustion is propagated under pulsed conditions (Table 4). For *o*- and *p*-toluidine perchlorates, transition of the combustion to pulsed conditions takes place with a jumpwise decrease of the rate; there is a small pressure range within which combustion can be propagated both at a uniform rate and with pulsation. For the perchlorates of *N*-methyl-aniline and *m*-toluidine, such jumps in the rate are not observed. Under pulsed conditions, benzylamine perchlorate starts to burn immediately. At high pressures, the combustion of all the isomers becomes uniform.

It can be noted that the introduction of a methyl group into aniline perchlorate, like a nitro group, has practically no effect on the value of the combustion rate. However, with the transition to benzylamine perchlorate, which also contains a benzene ring and is an isomer of the toluidines and *N*-methylaniline, but which does not have the properties of aromatic amines, the combustion rate falls sharply.

The dependences $u(p)$ for the diperchlorates of aromatic diamines are given in Fig. 8 and Table 5. All the compounds investigated burn with close rates, and have neither "discontinuities" on the curve of $u(p)$ nor sectors of pulsed combustion. However, at high pressures (above 200-300 atm), the combustion of the diperchlorates of phenylenediamine becomes unstable: there are jumps of the flame into the depths of the charge, leading to disintegration of the tube.

The rate of combustion of benzidine diperchlorate has been successfully measured only up to 160 atm due to the jumps of the flame, which already start at 100 atm. However, while with the diperchlorates of phenylenediamines, the jumps are accompanied by fragmentation of the casing, in the case of benzidine

TABLE 4

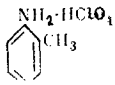
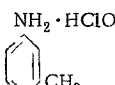
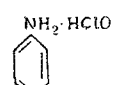
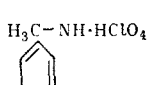
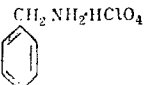
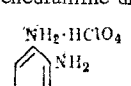
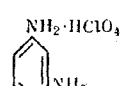
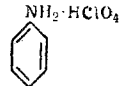
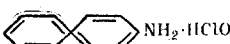
Substance	Pressure range, atm	Dependence of combustion rate (cm/sec) on pressure (atm)
o-Toluidine perchlorate 	1-18 16-130 130-400	$u=0,1p^{0,85}$ Pulsation $u=8,2 \cdot 10^{-3} p^{1,25}$
m-Toluidine perchlorate 	1-11 11-100 100-400	$u=8 \cdot 10^{-2} p^{0,8}$ Pulsation $u=2,2 \cdot 10^{-3} p^{1,16}$
p-Toluidine perchlorate 	1-18 18-90 90-400	$u=7,5 \cdot 10^{-2} p^{0,87}$ Pulsation $u=2,8 \cdot 10^{-3} p^{1,45}$
N-Methylaniline perchlorate 	1-11 11-200 200-400	$u=0,1p^{0,75}$ Pulsation $u=2,3 \cdot 10^{-5} p^{2,2}$
Benzylamine perchlorate 	3-120 130-200 200-400	Pulsation $u=2,2 \cdot 10^{-1} p^{0,37}$ $u=3,2 \cdot 10^{-4} p^{1,6}$

TABLE 5

Substance	Pressure range, atm	Dependence of combustion rate (cm/sec) on pressure (atm)
o-Phenylenediamine diperchlorate 	1-6 6-300	$u=0,1+4 \cdot 10^{-2} p^{1,4}$ $u=0,1+8 \cdot 10^{-2} p$
m-Phenylenediamine diperchlorate 	1-200	$u=0,18 \cdot p^{0,89}$
p-Phenylenediamine diperchlorate 	1-300	$u=0,23 \cdot p^{0,85}$
Benzidine diperchlorate 	1-12 12-160	$u=0,36 \cdot p^{0,4}$ $u=0,1 \cdot p^{0,93}$

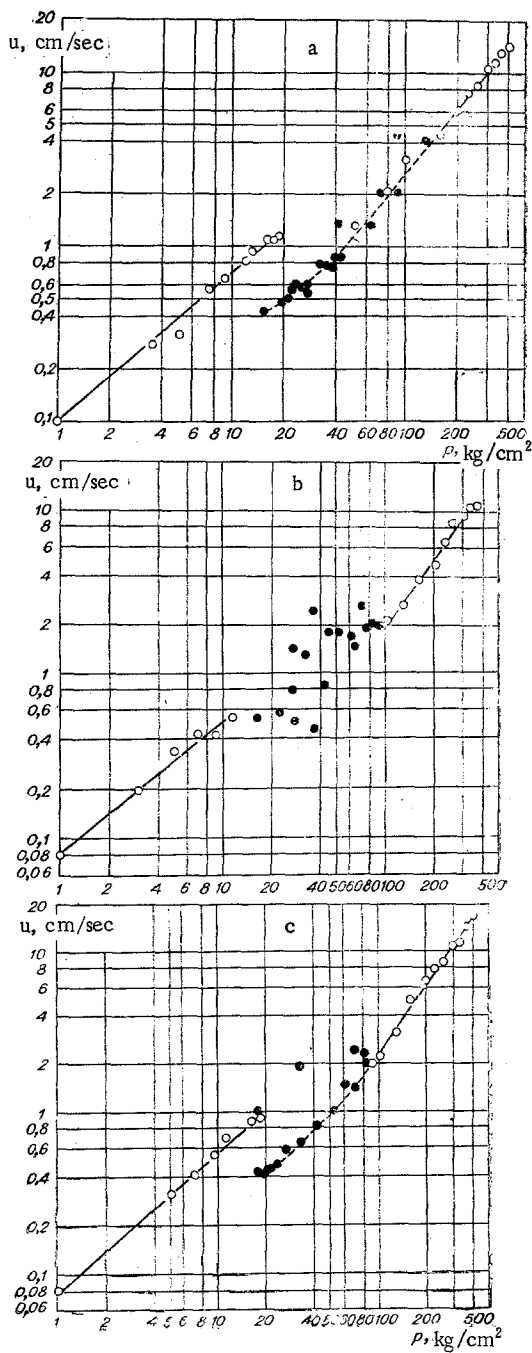


Fig. 8. Dependences $u(p)$ for the diperchlorates of aromatic amines: 1) *o*-phenylenediamine; 2) *m*-phenylenediamine; 3) *p*-phenylenediamine; 4) benzidine.

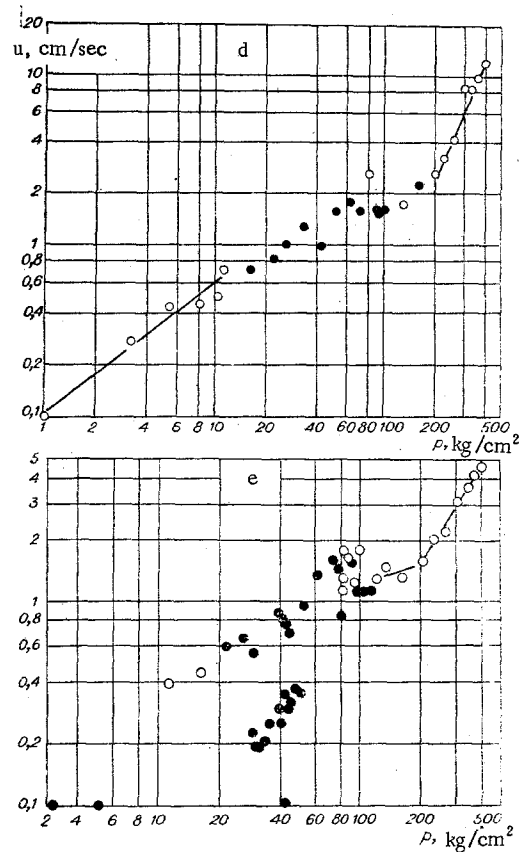


Fig. 7. Dependences $u(p)$ for isomers of the composition $C_7H_{10}NClO_4$: a) *o*-toluidine perchlorate; b) *m*-toluidine perchlorate; c) *p*-toluidine perchlorate; d) *N*-methylaniline perchlorate; e) benzylamine perchlorate. The filled circles represent combustion under pulsed conditions.

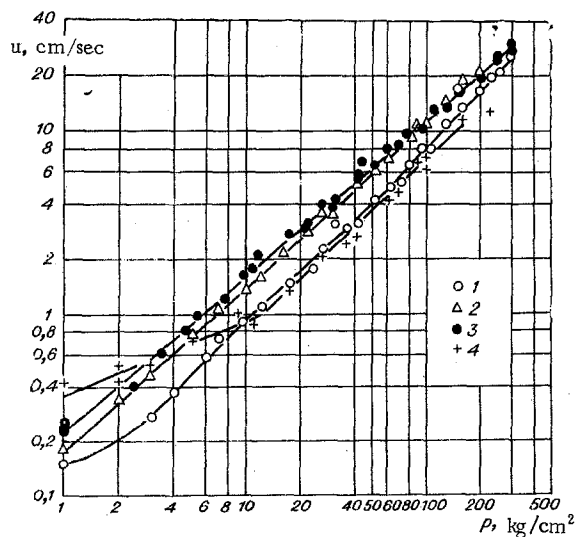


TABLE 6

Substance	Pressure range (atm)	Dependence of combustion rate (cm/sec) on pressure (atm)
Guanidine perchlorate $C(NH_2)_3ClO_4$	150—400	$u=7 \cdot 10^{-9} p^{3,45}$
Methylguanidine perchlorate $CH_3NHC(NH_2)_2ClO_4$	9—14 15—90 90—94 95—126 126—400	$u=7,4 \cdot 10^{-2} p^{0,8}$ Does not burn 0,22—0,25 cm/sec Does not burn $u=1,6 \cdot 10^{-4} p^{1,62}$
Aminoguanidine perchlorate $H_2N-C-NH-NH_2 \cdot HCO_4$ NH	5—25 26—180 180—260 260—400	$u=5,6 \cdot 10^{-2} p^{1,1}$ Does not burn $u=1,7 \cdot 10^{-7} p^{3,2}$ $u=6,9 \cdot 10^{-4} p^{1,7}$
Formamidine perchlorate $HC(NH_2)_2ClO_4$	3—21 22—47 47—200 200—260 260—400	$u=3,8 \cdot 10^{-2} p^{0,98}$ Does not burn $u=0,48+7,3 \cdot 10^{-8} p^{3,4}$ $u=1,4 \cdot 10^{-3} p^{1,53}$ $u=1,1 \cdot 10^{-1} p^{2,76}$

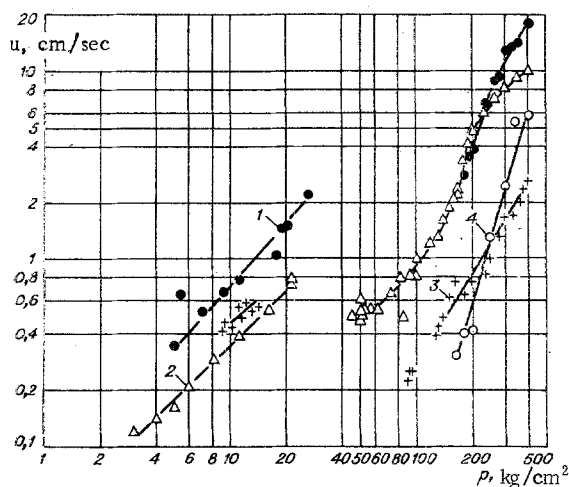


Fig. 9. Dependences $u(p)$ for the perchlorates of aminoguanidine (1), formamidine (2), methylguanidine (3), and guanidine (4).

15–40 atm methylguanidine perchlorate does not burn. At pressures of 91–94 atm, the charges burn with a strong pulsation; then there follows again a sector without combustion (94–126 atm). The combustion is renewed at a pressure above 126 atm and, up to 250 atm, is of a pulsed character.

The presence of a hydrazine grouping in guanidine perchlorate leads to a considerable increase in the rate. Aminoguanidine perchlorate burns faster than guanidine and methylguanidine perchlorates.

Perchlorates of Heterocyclic Amines. The dependence $u(p)$ for pyridine perchlorate (Fig. 10) is close in form to the analogous dependence for perchlorates of amidines and aliphatic amines. In the low-pressure region (2, 3–8 atm) the perchlorate burns stably. There then follows a pressure interval (8–70 atm) in which the combustion is not propagated. Above 70 atm, the rate rises rapidly with pressure ($u = 3,1 \cdot 10^{-4} p^{2,2}$); from 70 to 350 atm, the combustion proceeds with pulsation.

Piperazine diperchlorate ($O_4ClH \cdot HN \begin{array}{c} \diagup CH_2CH_2 \\ \diagdown CH_2CH_2 \end{array} NH \cdot HClO_4$) burns over the whole pressure range investigated.

From 1 to 90 atm, the rate increases slowly with pressure ($u = 2,2 \cdot 10^{-1} p^{0,8}$). Above 90 atm, the pressure exerts a stronger effect on the rate ($u = 3,9 \cdot 10^{-2} p^{1,2}$).

diperchlorate, the tube remains intact, and is merely thrown out of the holder. With the combustion of benzidine perchlorate, in contrast to the diperchlorates of phenylenediamines, there is formed a large amount of dense soot which, at high pressures, completely fills the tube and prevents the forming gases from flowing out. With an increase in the pressure, the density of the "plugs" made of soot increases, which probably also leads to jumps of the flame. It is of interest to note that benzidine diperchlorate burns at almost the same rate as the diperchlorates of phenylenediamines.

Perchlorates of Amidines. The dependences $u(p)$ for perchlorates of amidines are given in Fig. 9 and Table 6. Guanidine perchlorate does not burn on low pressures. Combustion starts only above 150 atm; up 350 atm, it proceeds under pulsed conditions. With the introduction of a methyl group into the guanidine molecule, combustion of the perchlorate is found possible at low pressures (9–14 atm). In the interval

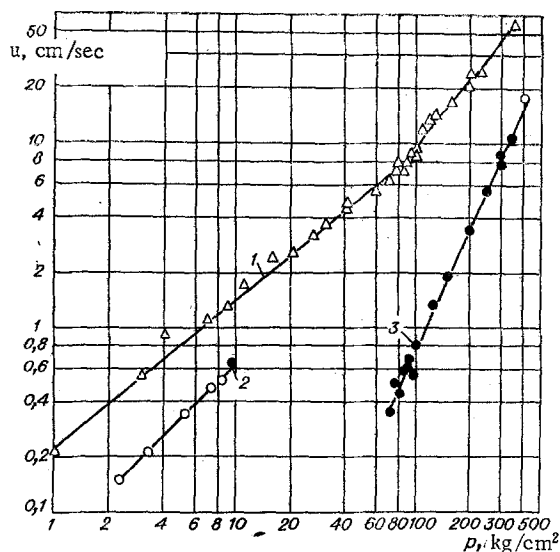


Fig. 10

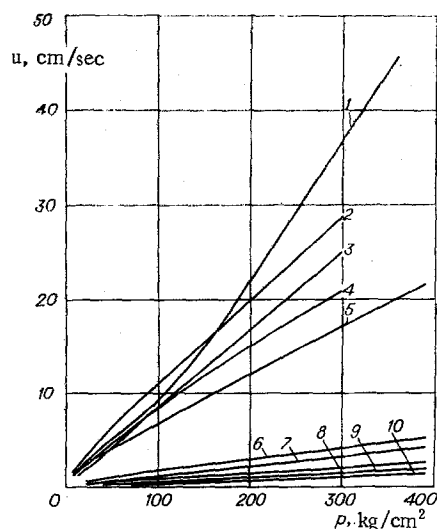


Fig. 11

Fig. 10. Dependence $u(p)$ for piperazine diperchlorate (1) and pyridine perchlorate Combustion of perchlorate under pulsed conditions (3).

Fig. 11. Dependences $u(p)$ for organic perchlorates and nitro compounds: 1) piperazine diperchlorate; 2) *p*-phenylenediamine diperchlorate; 3) *o*-phenylenediamine diperchlorate; 4) diethylenetriamine triperchlorate; 5) ethylenediamine diperchlorate; 6) hexogene; 7) pentaerythryl tetranitrate [PETN]; 8) Tetryl; 9) picric acid; 10) Trotyl [TNT].

Discussion of Results

A comparison between the combustion rates of explosive compounds in which the oxidizer is an NO_2 group and of organic perchlorates shows (Fig. 11) that the latter burn considerably more rapidly. This difference cannot be attributed to an increase in the heat of the explosive transformation, since even aniline perchlorate, having a value of Q_p of only ~ 600 kcal/kg, burns approximately three times faster than PETN, which has a heat of combustion of 1400 kcal/kg. The presence of the oxidizer Cl^{7+} in the molecule of the explosive substance leads also to a decrease in the stability of the compound [8], in comparison to substances containing NO_2 groups. With a lag of 5 sec (50 mg), for ethylenediamine diperchlorate the flash point is 335–340°C, while for ethylamine perchlorate it is 355–360°C. PETN and hexogene, under close conditions, ignite at 225, and 260°C, respectively [1]. It can therefore be assumed that the difference in the rates is mainly due to the fact that the combustion of the perchlorates is mainly due to the more active oxidizer.

The structure of the combustible part of the molecule also has an effect on the value of the rate: as a rule, the compounds which burn most rapidly are those which have the more reactive combustible part in their molecule. Thus, the perchlorates of toluidines and of *N*-methylaniline burn more rapidly than benzylamine perchlorate, which is isomeric with them; aminoguanidine perchlorate burns faster than guanidine perchlorate. However, while the difference in the combustion rates between perchlorates and nitro compounds is great, within a single class it is relatively small and is seldom more than 3–4 times if, of course, there is no significant decrease in the heat of the explosive transformation. The weak effect of the combustible part of the molecule on the combustion rate of explosive compounds is possibly associated with the fact that, in all cases, exactly the same elements, hydrogen and carbon, are oxidized; therefore, so long as there is no change in the organic part of the molecule, the reactivity of the combustible part changes considerably less than in a combination of nitrogen or chlorine with oxygen. It is therefore to be expected that, with a transition to compounds of the type PR_3HClO_4 , the combustion rate will increase sharply.

Investigation of a great number of organic perchlorates with a different structure of the combustible part of the molecule, as well as an examination of the combustion of several inorganic perchlorates [9–11],

TABLE 7

Substance	pK_a , base in aqueous solution [12]	Pressures at which there is no combustion of perchlorates, atm
Monoperchlorates		
Tetramethylammonium perchlorate	—	1—400
Guanidine perchlorate	13,6	<150
Methylguanidine perchlorate	13,4	<9; 15—90; 95—126
Formamidinium perchlorate	~12	<3; 22—47
Diethylamine perchlorate	11,1	<41; 194—199
Aminoguanidine perchlorate	11,0	<5; 26—180
Dimethylamine perchlorate	10,7	<1,5; 7—100
Ethylamine perchlorate	10,7	8—200
Methylamine perchlorate	10,6	<2; 11—60
n-Butylamine perchlorate	10,6	<120
Secondary butylamine perchlorate	10,6	<180
Isobutylamine perchlorate	10,4	<230
Ethylenediamine monoperchlorate	10,1(pK_a^1)	9—250
Trimethylamine perchlorate	9,8	<1,5; 7—290
Benzylamine perchlorate	9,3	<3
Ammonium perchlorate	9,3	<22; >250 [10]
Hydrazine monoperchlorate	8,5(pK_a^1)	7 [9]
Pyridine perchlorate	5,3	<2,3; 8—70
p-Toluidine perchlorate	5,2	None
m-Toluidine perchlorate	4,8	>
N-Methylaniline perchlorate	4,8	>
Aniline perchlorate	4,6	>
o-Toluidine perchlorate	4,5	>
m-Nitroaniline perchlorate	2,5	>
Polyperchlorates		
Hexamethylenediamine diperchlorate	10,1(pK_a^2)	110—330
Tetramethylenediamine diperchlorate	9,6(pK_a^2)	48—200
Ethylenediamine diperchlorate	7,0(pK_a^2)	None
Piperazine diperchlorate	5,7(pK_a^2)	>
Diethylenetriamine triperchlorate	4,3(pK_a^3)	>
Benzidine diperchlorate	3,4(pK_a^2)	>
p-Phenylenediamine diperchlorate	3,3(pK_a^2)	>
m-Phenylenediamine diperchlorate	2,7(pK_a^2)	>
o-Phenylenediamine diperchlorate	1,3(pK_a^2)	>
Hydrazine diperchlorate	—	> [9]

shows that the unusual form of the dependence $u(p)$ for the salts of perchloric acid (the presence of "discontinuities" or sectors of pulsed combustion) is rather the rule than the exception. However, in this case also, the structure of the combustible part of the molecule and, in particular, its basic properties, exert a considerable effect on the form of the dependence $u(p)$. Thus, if we arrange the salts in the order of a decrease in the basic properties of the cation (Table 7), it can be noted that for the perchlorates of strong bases ($pK_a > 5.2$ for monoperchlorates, and $pK_a > 7$ for polyperchlorates) either the absence of combustion at low pressures or the presence of "discontinuities" on the curve of $u(p)$ are characteristic. The perchlorates of aromatic monoamines, having a value of $pK_a \sim 5$, occupy, so to speak, an intermediate position: for these salts, there exists a pressure interval in which combustion is propagated only under pulsed conditions. Perchlorates obtained with a reaction between $HClO_4$ and cations having weak basic properties burn over the whole pressure interval. It should be particularly noted here that, while ethylenediamine diperchlorate burns over the whole pressure range investigated (the second molecule of $HClO_4$ joins itself to an amino group having weak basic properties, $pK_a^2 = 7.0$), ethylenediamine monoperchlorate does not burn in the interval 9–250 atm ($pK_a^1 = 10.1$). An analogous phenomenon is observed for hydrazine perchlorate [9]. Tetramethylenediamine diperchlorate, in which both amino groups have weak basic properties ($pK_a^1 = 10.8$; $pK_a^2 = 9.6$) since their mutual effect is weakened by the long hydrocarbon chain, does not burn in the interval 48–200 atm, while piperazine diperchlorate, which is close to it in composition, having relatively weak basic properties ($pK_a^1 = 9.22$; $pK_a^2 = 5.68$), particularly in the second amino group, burns at all pressures.

We note that, while for some substances, the "discontinuities" are characterized by a preliminary drop in the combustion rate, at the same time, for other substances, this is not observed. Renewal of the combustion is usually accompanied by a rapid rise in the rate (the index ν in the expression for the

combustion rate, as a rule, is much greater than unity). However, with an increase in the pressure, the rate of rise of the rate decreases. With an approach to the extinction region, both upward and downward, the combustion becomes pulsed.

Before trying to explain the unusual behavior of the salts of perchloric acid on combustion, let us recall that perchloric acid is the strongest of the inorganic acids. In anhydrous form, it has very strong oxidizing properties; practically all organic substances are ignited by contact with anhydrous perchloric acid. However, with an increase in the degree of dilution of HClO_4 , its oxidizing properties fall and, in the completely dissociated acid, under normal conditions oxidizing properties are almost absent. The first act in the decomposition of the salts is reversible dissociation into an amine and an acid; the dissociation temperature is higher the greater the value of the dissociation constant of the base in an aqueous solution [13].

We assume the following mechanism for combustion of the salts, close to the mechanism considered in [14]. Most of the heat for the propagation of the process is evolved in the liquid layer of the condensed phase as a result of the oxidation of the combustible contained in the molecule by perchloric acid. The temperature of the surface (T_S) is determined by the dissociation of the perchlorate into amine and perchloric acid, i.e., this is the temperature at which the saturated vapor pressure of the amine and of HClO_4 is equal to the external pressure. Here it must be borne in mind that, actually, the temperature of the surface will always be lower than the dissociation temperature due to a partial reaction taking place in the condensed phase with the formation of volatile products. The heat coming from the gas phase is expended only for dissociation of the undecomposed substance and for vaporization of the volatile reaction products.

With decomposition of a substance in a liquid layer of the condensed phase, the depth of the decomposition cannot exceed a certain limiting value (η_{\max}), under the condition that the rate of diffusion is much less than the rate of gas formation, since the solubility of the gaseous reaction products in a molten layer of the condensed phase has a definite limit. It follows from this that, at a given pressure, the condensed phase cannot be heated above a determined temperature $T_S^* = [(Q \cdot \eta_{\max})/c_p] + T_0$, where Q is the heat of reaction in the condensed phase; c_p is the heat capacity; T_0 is the initial temperature, as a result of the exothermic reactions taking place in it, if they are accompanied by the formation of volatile products.

According to the proposed mechanism, the basic condition for steady-state combustion is $T_S^* > T_S$. In addition, the dissociation temperature must be sufficiently high so that the exothermic oxidation reaction of the combustible can take place in the condensed phase.

The following relationships between T_S and T_S^* can be imagined:

1. The curve $T_S^*(p)$ always lies above the curve $T_S(p)$. In this case, in accordance with the proposed mechanism, combustion is possible at all pressures, with the exception of those at which, due to the low value of T_S , the oxidation reaction of the combustible by perchloric acid practically does not proceed in the condensed phase. This can be achieved for perchlorates of weak bases (aniline, nitroaniline, phenylenediamine, etc.) which burn over the whole pressure range.
2. The curve $T_S^*(p)$, at all pressures, lies below the curve $T_S(p)$; in this case, combustion due to reaction in the condensed phase is impossible. This type of substances probably includes tetramethylammonium perchlorate, the basic properties of whose cation approach in strength the hydroxides of the alkali metals. However, here it must be stipulated that dissociation of tetramethylammonium perchlorate into an amine and perchloric acid is impossible, and T_S must be the temperature of the boiling salt.
3. Curve $T_S^*(p)$ lies above curve $T_S(p)$ but, at some pressure, is tangent to it. Then, we may anticipate the presence of a region of unstable combustion near the point of tangency. These relationships obviously hold for the perchlorates of toluidines and for the perchlorate of N-methylaniline.
4. Curve $T_S^*(p)$ intersects the curve $T_S(p)$ twice and, in each segment, lies below it. In this case, we may expect the presence of "discontinuities" on the curve for $u(p)$. If the point of interaction of the curves in the low-pressure region corresponds to the value of T_S at which the oxidation reaction practically does not proceed, the perchlorate will burn only at high pressures. This type of relationship between T_S^* and T_S is obviously characteristic for the perchlorates of strong bases. However, it would be perfectly logical to expect that, with renewal of the combustion, its rate should be higher than that at which it ceased, since a higher pressure corresponds to a higher value of T_S . The curves of $u(p)$ should be analogous to the curve for methylamine perchlorate (see Fig. 1). However, as a rule, the combustion is renewed at exactly the

same rate at which it ceased. Immediately after the "discontinuity," the reaction proceeds under pulsed conditions (this can explain the low mean rate), and its rate increases very rapidly. With a rise in the pressure, the pulsation gradually disappears, and the dependence $u(p)$ becomes flatter and approaches its form before the "discontinuity." This type of picture can be followed for ammonium perchlorate [11] and for the perchlorates of formamidine and aminoguanidine. The strong dependence of the combustion rate on the pressure is obviously explained by the fact that, with an increase in the pressure, on the one hand, there is a decrease in the fraction of the time during which the combustion ceases, and, on the other hand, there is an increase in the rate of combustion of the layer of substance. This can be particularly easily noted for diethylamine, which starts to burn at a very low rate (0.01 cm/sec), while the time between combustion of layers of the substance reaches several seconds, during the course of which there is no movement of the front.

The presence of a "discontinuity" on the curve of $u(p)$ can also be explained somewhat differently. With an increase in the pressure and, consequently, in the value of T_s , the depth of the decomposition of perchlorate in the condensed phase will increase; this, in turn, leads to dilution of the HClO_4 by the oxidation products formed, one of which is water. With a determined pressure, such a degree of dilution of the HClO_4 may be attained that its oxidizing activity drops sharply and combustion stops. The less the heat of the explosive transformation of the salt, the lower the reactivity; and the greater the basicity of the amines, the greater is the probability that a "discontinuity" will appear on the curve of $u(p)$. Actually, "discontinuities" on the curves are characteristic for the perchlorates of strong bases (see Table 7), but are not observed with the combustion of the perchlorates of aromatic amines, the combustible part of whose molecule has weak basic properties and enters easily into oxidation reactions (for example, it is even oxidized by the oxygen of the air at room temperature). Renewal of the combustion is probably connected with the fact that, at high pressures and, consequently, high values of T_s , even diluted HClO_4 is capable of oxidizing the combustible at a high rate.

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