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Thermal analysis of binary mixtures of CaO, CaO_2, $Ca(OH)_2$, and $Mg(OH)_2$ with sodium and potassium perchlorates

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The catalytic activity of magnesium oxide, calcium oxide, and calcium peroxide in reactions of dioxygen evolution from sodium and potassium perchlorates has been studied. Additives of CaO facilitate the complete decomposition of perchlorates within the same temperature range as that found for additives of Mn, Co, Ni, and Cu oxides. The data on the low catalytic activity of calcium oxide in the decomposition of perchlorates are attributed to a systematic error caused by uncontrolled hydration of the CaO surface. It has been shown that CaO_2 can be used as a convenient precursor of CaO in pyrotechnic systems.

Key words: perchlorates, thermal analysis, heterogeneous catalysis, calcium oxide, magnesium oxide; calcium peroxide, calcium hydroxide, magnesium hydroxide.

Compounds containing alkaline-earth elements are used as absorbers of heat and toxic admixtures appearing upon thermal decomposition of pyrotechnic materials containing chlorates and perchlorates.[1–3] BaO_2 and $Ba(OH)_2$ are most often used for these purposes, because they efficiently prevent the evolution of dichlorine and catalyze the decomposition of the salts mentioned.[3,4]

Stable nonhygroscopic barium peroxide is still of interest as a component of modern pyrotechnic compositions[5,6]; however, its inherent high toxicity and high molecular weight create several inconveniences. In this connection, there were attempts to alter BaO_2 with compounds of light alkaline-earth metals (LAEM), including $MgFeO_3$,[7] magnesium and calcium oxides, hydroxides, and carbonates[8,9] as well as magnesium and calcium peroxides.[9,10]

The application of LAEM oxides and hydroxides in pyrotechnic sources of dioxygen has been prompted[8–12] by the ability of these compounds to absorb toxic admixtures and excessive heat. In these cases, it was suggested to accelerate the decomposition of the dioxygen source by oxides of d-elements, for example, cobalt oxide.[8] Such an approach to the development of pyrotechnic compositions is directly related to the data on the low catalytic activity of magnesium and calcium oxides toward processes of dioxygen transfer from perchlorates[13–16] and chlorates[13,17–22] to the environment, which was theoretically explained in several works.[13–22]

The idea to study repeatedly the two-component mixtures of perchlorates with magnesium- and calcium-containing compounds has raised as a result of the analysis of the experimental data presented in one of these works (Ref. 14). It follows from the description of the experimental procedure[14] that, before mixing, a portion of d-metal oxides was calcinated to remove water and hydroxide groups. In the case of CaO, the

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initial material was not subjected to a similar thermal treatment.

It is known that the presence of hydroxides on the surface affects substantially the catalytic activity of oxides, in particular, magnesium and calcium oxides.[23] The high rate of transport of the products formed in the chemical decomposition of $Mg(OH)_2$ and $Ca(OH)_2$ [24–27] results in efficient filling of the external surface of a granule by hydroxide groups, which can be manifested in a pseudo-first order of dehydration.[28] Therefore, a sufficiently high degree of drying is required for the reactivity of the oxide surface. The results described previously[14] have left some doubts concerning the quality of calcium oxide used. In this connection, the comparative study of the catalytic effect of MgO, CaO, CaO_2, $Mg(OH)_2$, and $Ca(OH)_2$ on the decomposition of sodium and potassium perchlorates has been performed in this work.

Experimental

$Ca(OH)_2$ and $Mg(OH)_2$ (analytically pure grade) and NiO (specially pure 10-2 grade) calcined at 600 °C were used.

Initial perchlorates were prepared by double recrystallization from the corresponding reagents (reagent grade) followed by drying. $NaClO_4$ was dehydrated by heating in a rotary evaporator with vacuum pumping at a temperature lower than 320 °C and with a heating rate of 6 °C min^{-1}. The dried sample in a hermetically closed flask was cooled slowly in air. A similar method for the preparation of perchlorates has been described previously[29] for $Ca(ClO_4)_2$. $KClO_4$ was dehydrated at 120 °C and atmospheric pressure.

Two samples of CaO were used. The first of them was obtained by the calcination of CaO_2. The sample was placed into a furnace preliminarily heated to 900 °C and then cooled in this furnace to 700 °C for 10 min in air (*cf.* Ref. 30).

In the second case, CaO_2 was added to the initial perchlorates.* Almost anhydrous CaO is formed upon thermal decomposition according to the reaction $2\ CaO_2 = 2\ CaO + O_2$ (see Ref. 31). The reaction occurs at the heating rate of 10 °C min^{-1} in the temperature range from 330 to 460 °C (Fig. 1).

The content of the perchlorate ion was determined by the weight method, precipitating with nitron acetate. The content of the chloride ion was determined by Volgard titration. The total content of chloride and chlorate was determined after the reduction of the latter to chloride by SO_2.

The amount of active oxygen in a sample of calcium peroxide was determined by permanganatometry.[33] A decrease in mass of the CaO_2 sample due to the loss of oxygen on heating was measured by gravimetry.

Decomposition of initial substances and their mixtures was studied by thermal analysis on a Derivatograph Q1500D setup with the heating rate of 10 °C min^{-1} in 6-mm quartz crucibles. The masses of weighed samples ranged from 70 to 100 mg. Thermogravimetric (TGA) and differential thermal (DTA) analyses were carried out under such conditions of heat exchange between a sample and environment that the rate of dioxygen evolution would increase linearly at the exothermic stage, when the temperature of the outer wall of the crucible with a sample increases linearly.[34,35]

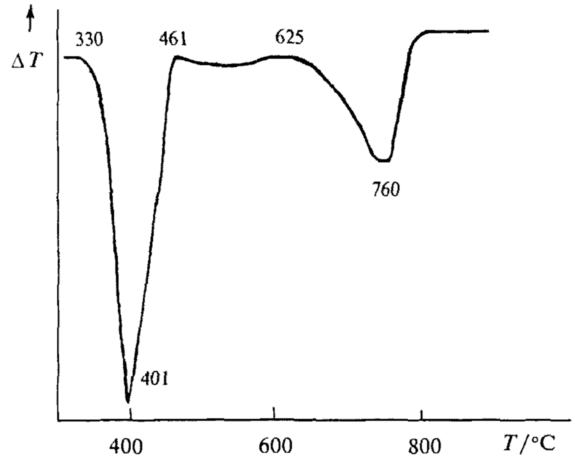

Fig. 1. DTA curve for CaO_2.

Diffractograms of powders were obtained on a DRON-3M setup (Institute of New Chemical Problems of the RAS) for samples as pastes with fluorinated oil, which were placed into the quartz cell protected from moisture by the fluoroplastic film 0.15 μm thick.[36] IR spectra (suspensions in Vaseline oil) were recorded on a UR-20 spectrometer.

Results and Discussion

The results of chemical, X-ray diffraction, spectroscopic, and thermal analyses of the initial substances are presented below.

The sample of calcium peroxide contains 95.7 % of CaO_2. The main admixture was 4 % of $CaCO_3$, which decomposes in the temperature range from 625 to 760 °C (see Fig. 1); traces of chloride ions are also observed.

The diffractograms of calcium oxide prepared by the thermal impact of CaO_2 and calcium oxide obtained by the thermolysis of CaO_2 during the linear heating with the rate of 10 °C min^{-1} turned out to be similar and correspond to the standard diffractogram,[37] which agrees with the results of Ref. 30 (explosive decomposition of $Ca(OH)_2$ and $CaCO_3$) and the data of X-ray diffraction analysis[31] of the solid products of decomposition of CaO_2.

The thermal analysis of calcium hydroxide shows the presence of low amounts of carbonate admixtures (Fig. 2, curve *1*) that decomposes at ~700 °C. The DTA curve of the initial $Mg(OH)_2$ has a minimum at 420 °C (see Fig. 2, curve *2*), which is close to the values obtained previously.[14] No additional thermal effects are observed up to 900 °C.

Chemical analysis of the samples of sodium and potassium perchlorates testifies that they contain 99.8 wt. % of the main substance. The diffractograms and the IR spectroscopy data are typical of anhydrous $KClO_4$ and $NaClO_4$ (see Refs. 37 and 38).

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* Initial CaO_2 obtained by the exchange reaction of $CaCl_2$ with an aqueous-ammonia solution of H_2O_2 (see Ref. 32) was kindly provided by D. G. Lemesheva (N. S. Kurnakov Institute of General and Inorganic Chemistry of the RAS).

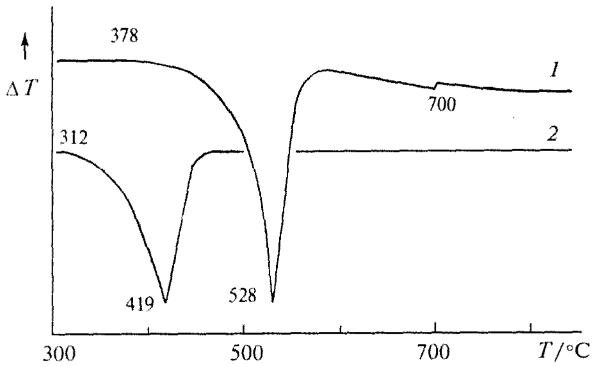

Fig. 2. DTA curves for calcium (*1*) and magnesium (*2*) hydroxides.

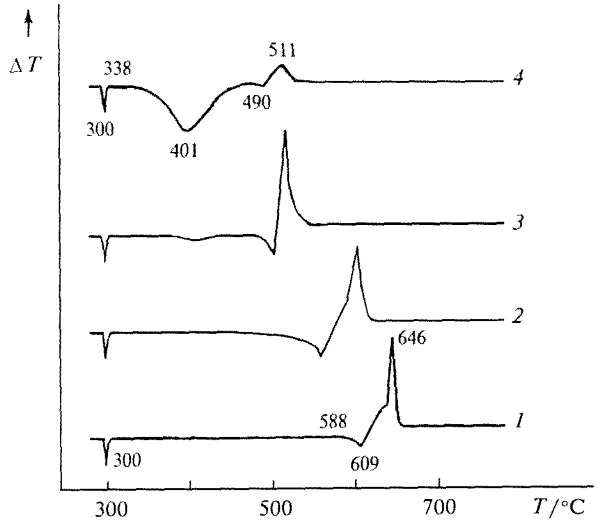

Fig. 3. DTA curves for $KClO_4$ (*1*) and two-component mixtures (*2—4*): *2*, 1 g-mol $KClO_4$ + 0.01 g-mol CaO_2; *3*, 1 g-mol $KClO_4$ + 0.5 g-mol CaO_2; *4*, 1 g-mol $KClO_4$ + 10 g-mol CaO_2.

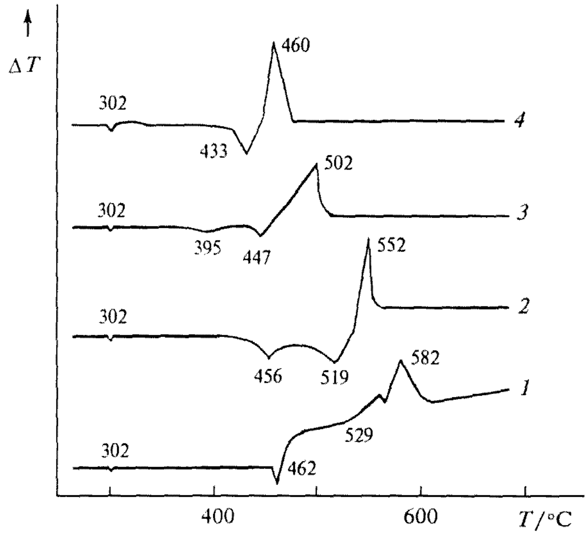

Fig. 4. DTA curves for $NaClO_4$ (*1*) and two-component mixtures (*2—4*): *2*, 1 g-mol $NaClO_4$ + 1 g-mol $Ca(OH)_2$; *3*, 1 g-mol $NaClO_4$ + 1 g-mol CaO_2; *4*, 1 g-mol $NaClO_4$ + 1 g-mol CaO.

The results of thermal analysis of perchlorates (Fig. 3) differ somewhat from the standard data.

For potassium perchlorate placed into a quartz crucible (see Fig. 3, curve *1*), the endothermic effect at 300 °C corresponds to the polymorphous transition of $KClO_4$.[39] Decomposition occurs in the 585—655 °C temperature range, which is 20—30 °C higher than that observed in several known works; however, it is very close to the result obtained by Anderson and Freeman.[40] This disagreement is likely related only to the conditions of thermal analysis,[34,35] which reduce to minimum the possibility of noncontrolled local overheating of the material studied in the course of analysis.

The polymorphous transformation of anhydrous $NaClO_4$ is accompanied by the endothermic effect with a minimum at 302 °C (Fig. 4, curve *1*), which is 5—6 °C lower than the known reference values.[41—43] Nevertheless, the temperature obtained almost coincides with the lower boundary of this transition determined on cooling[44] and the data[14] standardized by the phase transition temperature of $KClO_4$ (300 °C).[39] (The authors of Ref. 14 observed the transformation of $KClO_4$ from the orthorhombic modification into the cubic modification at 310 °C, and the corresponding transition of $NaClO_4$ occurs at 313 °C.)

The disagreement of 5—6 °C between the temperature obtained for the polymorphous transformation of $NaClO_4$ and the literature data (Refs. 41—43) cannot be explained by systematic error. It is likely that this difference is caused by the complex character of the polymorphous transformation of $NaClO_4$ (see Refs. 42, 44, and 45).

The formation of the liquid phase for the $NaClO_4$ samples placed into the quartz crucible results in the appearance of the minimum at 462—463 °C on the DTA curve (see Fig. 4). No gas evolution was observed during this process on either the curves of mass loss (TGA) or curves of the rate of its change (DTG). A noticeable decomposition (on the DTG curves) begins only at 482—485 °C. At the higher temperatures, the run of the process agrees well with that described by Markowitz and Boryta (Ref. 46).

The coincidence (or good correspondence) of the observed pattern of decomposition of $NaClO_4$ and $KClO_4$ with the results of Refs. 40 and 46 makes it possible to consider that these peculiarities of the behavior of perchlorates exert no substantial effect on the reactivity of the substances prepared for the study. Therefore, the results of this work can be compared quantitatively with the data obtained previously[13—22] on the catalytic activity of magnesium and calcium oxides toward decomposition of chlorates and perchlorates.

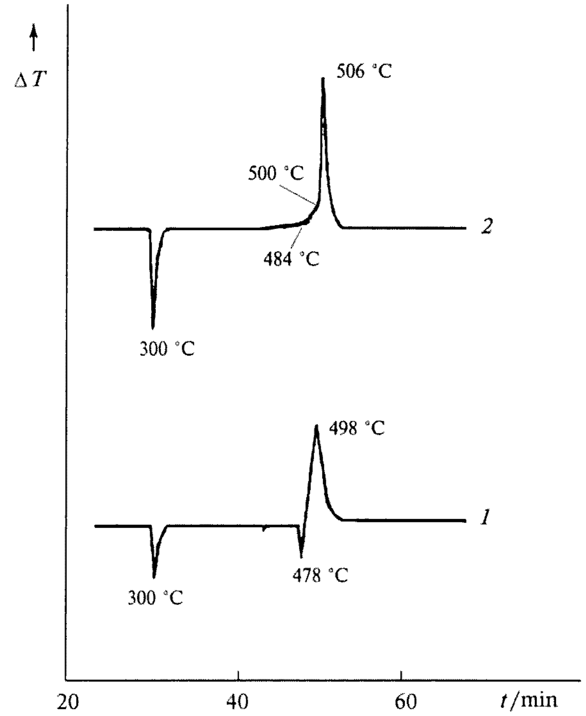

Fig. 5. DTA curves for two-component mixtures: *1*, 1 g-mol $KClO_4$ + 1 g-mol CaO; *2*, 1 g-mol $KClO_4$ + 1 g-mol NiO.

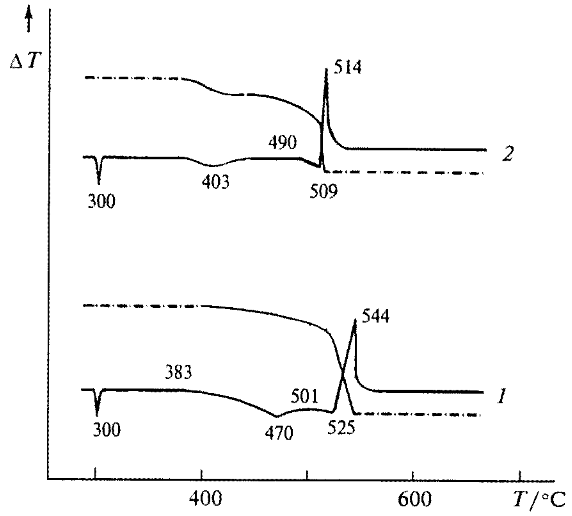

Fig. 6. Thermograms of two-component mixtures: *1*, 1 g-mol $KClO_4$ + 1 g-mol $Ca(OH)_2$; *2*, 1 g-mol $KClO_4$ + 1 g-mol CaO_2. The DTA curve is shown by the solid line, and the TGA (loss of mass) curve is shown by the dotted line.

The thermograms of the two-component $KClO_4$—CaO_2 and $NaClO_4$—CaO_2 systems are presented in Figs. 3—5. The process of dioxygen evolution can be divided into two qualitatively different stages by the character of heat effects. It is established by chemical, X-ray diffraction, and IR spectroscopic analyses that $NaClO_3$ or $KClO_3$ is accumulated in the presence of CaO at the first, endothermic stage, while the final product, NaCl or KCl, is formed at the second, exothermic stage in the presence of CaO as well.

The effect of calcium peroxide on the process of dioxygen evolution from sodium and potassium perchlorates are manifested clearly by the decrease in the temperatures of its beginning and end (see Figs. 3 and 4). For example, for the two-component $KClO_4$—CaO_2 system with a 1 : 1 molar ratio, the temperature of the end of decomposition of the sample is 130 °C lower than that for the decomposition of the pure salt (see Fig. 3, curve *1*; Fig. 6, curve *2*), and it is 80 °C lower for the same mixture of $NaClO_4$ with CaO_2 (see Fig. 4, curves *1* and *3*).

Anhydrous calcium oxide is the acting agent in these reactions. It forms upon thermolysis of CaO_2 even before the beginning of decomposition of perchlorate, and then it remains as one of the products.

It is noteworthy that in the presence of anhydrous CaO obtained from CaO_2 by implosive decomposition the temperature of the complete decomposition of potassium perchlorate can decrease approximately in the same manner as under the action of nickel oxide (see Fig. 5). The thermal stability of sodium perchlorate also decreases considerably in the presence of anhydrous CaO. For example, the exothermic stage of decomposition of the initial sample for the mixture (1 mol $NaClO_4$ + 1 mol CaO) at a heating rate of 10 °C min^{-1} is observed at 430—460 °C (see Fig. 4, curve *4*).

Despite numerous data[13—22] on the low catalytic activity of MgO and CaO in the reactions of dioxygen evolution from a perchlorate-chlorate source, the results obtained (see Figs. 3—5) testify that calcium oxide can be considered as one of the efficient catalysts of this process.

Equimolar two-component mixtures of $NaClO_4$ and $KClO_4$ with $Ca(OH)_2$ and $Mg(OH)_2$ have been studied to reveal the reason for the disagreement between the results of the present work and the literature data (Refs. 13—22).

The thermograms of the mixture of potassium perchlorate and calcium hydroxide (see Fig. 6) agree well with the experimental data[14] obtained for the mixture of $KClO_4$ with the CaO sample of the same molar ratio (1 : 1). The beginning of the rigorous dioxygen evolution is observed, as previously,[14] at 525 °C, *i.e.*, in the temperature range where the decomposition of $Ca(OH)_2$ is nearly completed (see Fig. 4, curve *2*). In our experiments, the loss of mass at 515—520 °C corresponds to 20 % of the total decrease in the mass of the sample, which also correlates well with the content of hydroxide groups in the initial mixture.

Thus, it can be assumed that the results described in several works[13—15] contain the systematic error caused by hydration of CaO. Anhydrous calcium oxide exhibits a considerably higher catalytic activity, even if it is formed from calcium peroxide with some delay (see Fig. 4 and Fig. 6, curve *2*).

The effect of hydroxide groups on the catalytic decomposition of perchlorates can be observed, when the temperature range of the exothermic decomposition of $NaClO_4$ and $KClO_4$ in the presence of $Ca(OH)_2$ and $Mg(OH)_2$ is compared with the data on dioxygen evolution upon thermolysis of mixtures of $NaClO_4$ and $KClO_4$ with MgO and CaO. The mixtures of magnesium and calcium oxides and hydroxides with NH_4VO_3 have been studied previously[23] with the analogous purpose. The comparison (Table 1) shows that the catalytic activity of MgO obtained by the decomposition of $Mg(OH)_2$ at 390—410 °C is considerably lower than that of CaO. This is evidenced by the temperatures of the beginning and the maximum of the exothermic effects (see Table 1, runs *1—4*). However, the comparison of the effects of $Ca(OH)_2$ and $Mg(OH)_2$ (see Table 1, runs *5* and *6*) shows that the shift caused by an additive of the calcium-containing compound is quite opposite in this case: it does not decrease, but increases the temperature. The higher thermal stability of $Ca(OH)_2$ (see Fig. 2) results in the situation when $Ca(OH)_2$, unlike $Mg(OH)_2$, has not managed to leave the oxide surface, and, therefore, the additive of $Ca(OH)_2$ accelerates the process of dioxygen evolution from the perchlorate source less efficiently than $Mg(OH)_2$.

It also follows from the results of this work that peroxide groups can prevent the manifestation of the catalytic activity of CaO_2 in the reactions of decomposition of perchlorates and chlorates. This is well seen from the comparison of the DTA curves of the two-component mixtures of $NaClO_4$ and $KClO_4$ with CaO and CaO_2 (see Figs. 3—5). At the same time, it is known[3,4] that barium peroxide catalyzes decomposition of chlorates and perchlorates. This specific feature of CaO_2 can be related to the low enthalpy of formation of calcium superoxide in a solid solution with peroxide. For example, the value of the standard enthalpy of formation of superoxide is -596.8 ± 4.4 kJ mol^{-1} for CaO_4 in CaO_2, while it is -655.00 ± 1.5 kJ mol^{-1} for pure CaO_2 (see Ref. 47), which almost rules out the oxidation of calcium peroxides by sodium and potassium perchlorates. This process is more probable in the case of barium peroxide.[48]

Table 1. Temperature range of exothermic decomposition of potassium and sodium perchlorates in the presence of magnesium and calcium oxides and hydroxides

Run	Mixture*	Beginning of exothermic decomposition, T_1/°C	End of exothermic decomposition, T_2/°C
1	$KClO_4$ + MgO	541	562
2	$KClO_4$ + CaO	478	498
3	$NaClO_4$ + MgO	518	528
4	$NaClO_4$ + CaO	433	460
5	$NaClO_4$ + $Mg(OH)_2$	518	528
6	$NaClO_4$ + $Ca(OH)_2$	519	552

* The molar ratio was 1 : 1.

The results of this work make it possible to evaluate the prospects for using oxides, peroxides, and hydroxides of some LAEM in catalytic decomposition of perchlorates and chlorates. This evaluation differs from the commonly accepted one.[8—22] Hydroxides, $Mg(OH)_2$ and $Ca(OH)_2$, can find application not only as additives for absorbing heat and toxic admixtures[8—12] but as substances accelerating the decomposition of oxidants that are traditional for pyrotechnic materials.

Oxides, MgO and CaO, will probably find restricted application as catalysts of thermolysis due to their hygroscopic nature.

Calcium peroxide is of the most interest. The use of CaO_2 additives for decreasing the temperature of decomposition of perchlorate and chlorate dioxygen source in the absence of noticeable formation of metalates favors the decrease in dichlorine admixtures in the gas evolved. In addition, CaO_2 is characterized by low toxic products of thermolysis, a low molecular weight, a rather high stability in a moist atmosphere.[48] These properties allow one to consider CaO_2 as a promising material for modern pyrotechnic dioxygen generators.

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